IDENTIFYING THE MAJOR SPILLED OIL CONSTITUENTS AND FATE IN HARSH OFFSHORE ENVIRONMENTS

by

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ABSTRACT

The behaviour and fate of spilled oil in harsh marine environments, such as the North Atlantic and the Arctic Ocean are complex due to environmental factors and the composition of the crude. In order to develop appropriate oil spill prevention and management methods, we must first understand how the oil behaves in these harsh environmental conditions. This study focuses on determining the fate of oil in harsh marine environments by first identifying target compounds in the oil that can be used to determine the fate of a spill. This thesis presents the partitioning behaviour of six polycyclic aromatic hydrocarbons (PAHs), which represent different groups, and phenols in cold conditions. The smallest PAH, naphthalene, dominated in terms of concentration in water accommodated fraction (WAF) of oil, while the larger ringed PAHs presented at lower concentrations. The smallest oil-water partition coefficient was recorded by phenol which partitioned into the seawater more quickly than PAHs. The partitioning of larger PAHs was slower and they indicated high partition coefficients. The oil partitioning increased slightly as temperature increased from 4 ^{o}C to 15 ^{o}C. The oil loading (0.1 g/L to 10 g/L) also contributed in deciding the concentrations in water. The use of chemical dispersants is a common response to spills. This study identified that chemical dispersants can change the fate of an oil spill by increasing the availability of oil in seawater. The concentration of larger PAHs such as pyrene and chrysene increased significantly with the application of dispersants. The information obtained are used in developing a molecular imprinted polymer (MIP) sensor to identify oil spills in the North Atlantic Ocean.

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List of Symbols, Nomenclature or Abbreviations

^{o}C	Degrees Celsius
PA	Peak area of the chromatogram
API	American Petroleum Institute
ASTM	American Society for Testing and Materials
atm	Atmospheric pressure
BTEX	Benzene, toluene, ethylbenzene, xylene
C	Intercept
CEWAF	Chemically enhanced water accommodated fraction
C_l	The concentration of a substance in an organic liquid phase
cP	Centipoise
CROSERF	Chemical Response to Oil Spill Ecological Effects Research Forum
C_s	Concentration of an analyte in stock solution
C_T	Resultant concentration of an analyte in the final sample
C_w	The concentration of a substance in water phase
$C_{w,sat}$	The saturated solute concentration in pure water
C_x	Concentration of an analyte in the oil sample
DCCLC	Dynamic coupled column liquid chromatography
DCM	Dichloromethane
FID	Flame ionization detector
g	Gram
GC-MS	Gas chromatography-mass spectrometry

h	Hour
HCl	Hydrochloric acid
HKF	Helgeson-Kirkham-Flowers
HPLC	High performance liquid chromatography
IR	Infrared
IS	Internal standard
P'	Constant of proportion
K	Partition coefficient
K'	Setschenow constant or salting constant
K_{lw}	Organic liquid-water partitioning coefficient of a substance
K_{ow}	Octanol-water partition coefficient
$K_{ow,salt}$	Octanol water partition coefficient corrected for the salinity
L	Liter
m	Gradient
m/z	mass-to-charge ratio
NaCl	Sodium chloride
Pa	Pascal
PAH	Polycyclic aromatic hydrocarbon
ppb	Parts per billion
ppm	Parts per million
ppt	Parts per thousand
PTFE	Polytetrafluoroethylene
R	Universal gas constant

rpm	Rotations per minute
SD	Standard deviation
s	Second
SG	Specific gravity
SIM	Selective ion monitoring
SS	Stock solution
SVOC	Semi-volatile organic compound
T	Temperature in Kelvin
TPH	Total petroleum hydrocarbons
UCM	Unresolved complex mixture
UK	United Kingdom
US	United States
US EPA	United States Environmental Protection Agency
UV	Ultraviolet
VOC	Volatile organic compound
VS	Volume of the stock solution
VT	Final volume of the resultant sample to be analyzed
V_x	Volume of the oil sample
WAF	Water accommodated fraction
α	Confidence interval
ΔH	Enthalpy
ΔS	Entropy

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1. Literature review

1.1. Introduction

The behaviour and fate of oil spills in harsh offshore environments, such as North Atlantic and Arctic is complex due to environmental factors and the composition of the crude oil. Low temperatures, ice cover, high winds, waves and also the deep water column combined with remote location complicate the mitigation and management of oil spills (CAPP, 2010; Venkatesh et al., 1990). The typical processes that influence the oil behaviour in the environment, and hence direct the response, such as evaporation, dispersion, microbial degradation (Siron et al., 1993) and photochemical oxidation, occur at much slower rates in cold/harsh environments, possibly resulting in persistence of some oil compounds. In addition, ice cover is known to alter the oil spreading pattern relative to open water (Izumiyama et al., 2002; Yapa and Chowdhury, 1989), but the process is not well understood. The size of any oil slick and degree of spreading will be reduced in ice. Oil-ice interfacial force (Kawamura et al., 1986), gravity and oil viscosity (Yapa and Weerasuriya 1997) are factors that determine the spreading of oil on ice. Oil entrainment in interstitial spaces between ice crystals (depending on the porosity of ice) temporarily removes oil from water during the winter season. As ice melts, the oil is added again to the seawater (Petrich et al., 2013). Wind and sea currents control the encapsulation of oil in ice and help to spread oil immediately after a spill (Chen et al., 1974). However, Chen et al. (1974) noted the oil is almost stationery at temperatures below -19 ^{o}C. Yapa and Chowdhury (1989) stated oil recovery becomes more complex in ice due to the inability to locate the oil slick under ice and encapsulation of oil in ice.

Although there is published work on oil spills in temperate open water conditions, the available knowledge of oil behaviour in harsh ocean conditions is still lacking (Brandvik and Faksness, 2009; Reitsma et al., 2013). As noted above, the behaviour directs the response and therefore better information on oil spill behaviour in these regions will inform response and management methods.

Response to oil spills vary from mechanical (e.g. booms), to chemical (e.g. dispersants), to thermal (e.g. in-situ combustion). However, in remote locations and/or energetic oceans, chemical dispersants are commonly used (Lessard and DeMarco, 2000). Chemical dispersants reduce the oil - water interfacial tension and help form oil-surfactant micelles that are easily dispersed into the water column preventing oil slicks formation (National Research Council U.S., 2005). These micelles can be 1 to 70 μm in diameter and extend into the water column up to 10 m deep (Lunel, 1998; Wells et al., 1982). Torrey Canyon oil spill in UK in 1967 (Lessard and DeMarco, 2000), Valdez oil spill in Alaska in 1989 and Deepwater Horizon oil spill in Gulf of Mexico in 2010 (Skogdalen and Vinnem, 2012) are some of the incidents where chemical dispersants were used as a clean-up technique in the North sea.

1.2. Crude oil constituents and their presence in seawater

Crude oil is compositionally complex, made up of a large number of compounds ranging from light hydrocarbons to heavier asphaltenes and waxes, inorganic and organic sulphur, nitrogen containing compounds and metals among other compounds. As a result,

the fate of compounds in an oil spill varies widely depending on their polarity, solubility, seawater temperature etc. (Wang and Fingas, 1997).

Due to the complexity in assessing fate and impact, compounds that make up oil are grouped according to chemical properties. Aromatic hydrocarbons are of particular interest due to their potential immunotoxicity and carcinogenicity. The group of volatile organic compounds (VOCs), BTEX (benzene, toluene, ethylbenzene and xylene) have been detected in water accommodated fractions of fresh oil spills (Reynaud and Deschaux, 2006; Wang and Fingas, 1997). In addition, the alkylated homologues, light alkanes and saturated hydrocarbons such as cyclopentane and cyclohexane have been found in light and fresh crude oil spills (Faksness et al., 2008). Taylor et al. (2010) found that light-weight hydrocarbons like mono or di-aromatics are readily water soluble (octanol/water partition coefficient (log K_{ow}) is less than 4) and become saturated in the water column within a few hours of an oil spill.

Polycyclic aromatic hydrocarbons (PAHs) are more persistent and toxic relative to single ring aromatics and therefore PAH composition is a key indicator of oil toxicity (Eom et al., 2007; Whitehouse, 1984). Two to three ring PAHs including phenanthrene, fluorene, dibenzothiophene (sulfur heterocycles) , biphenyl and anthracene (Faksness et al. 2008; Reddy et al. 2012) and four to six rings including pyrene, chrysene, fluoranthene, perylene etc (Christensen and Tomasi, 2007; Faksness et al., 2008; Reddy et al., 2012; Whitehouse, 1984) were identified as semi volatile organic compounds (SVOCs) present in oil. The United Sates Environmental Protection Agency (US EPA) specified priority pollutants under the clean water act. Table 1-1 shows 16 of the PAHs selected by Yan et al., (2004) in their study.

Table 1-1: 16 of the US EPA priority pollutants selected by Yan et al., (2004)

Naphthalene	Pyrene
Acenaphthene	Fluoranthene
Acenaphthylene	Benzo[b]fluoranthene
Phenanthrene	Benzo[k]fluoranthene
Fluorene	Benzo[a]pyrene
Anthracene	Indeno[1,2,3-cd]pyrene
Benz[a]anthracene	Benzo[ghi]perylene
Chrysene	Dibenz[a,h]anthracene

The water accommodated fraction (WAF) of crude oil is used in laboratory scale experiments to study oil bahaviour in water. The Chemical Response to Oil Spill Ecological Effects Research Forum (CROSERF) define WAF as a laboratory medium that is prepared by mixing less water soluble materials like crude oil under low-energy mixing without creating a vortex. WAF preparation does not essentially include any particle removing steps such as filtration, centrifugation etc. (Singer et al. 2000). The WAF will reflect the maximum equilibrium concentration possible in the water phase (Barron and Ka'aihue, 2003; Faksness et al., 2008).

A study of the initial water column after the Deepwater Horizon spill by Reddy et al. (2011) identified BTEX, mono-cyclic and poly cyclic aromatics, n-alkanes, branched alkanes. Benzene is highly water soluble and can accumulate in the deep water column but less so on the water surface. Due to their non-polar and hydrophobic nature, PAHs

show less solubility in fresh water, which is further decreased in seawater (Xie et al., 1997). However C_0 to C_4 Phenols and naphthalenes are highly water soluble compared to other petroleum specific aromatics and hence are abundant in WAF (Paul et al., 1997). Yim et al. (2011), in their study of un-weathered oil, found that naphthalene accounted for more than 56% of total PAHs. Dibenzothiophenes and phenanthrenes were the second and third most abundant constituents in terms of percentage by mg/g respectively. Pristane and phytane are isoprenoid hydrocarbons also identified as possible target analytes in oil spill studies (Lewis et al., 2010).

Total petroleum hydrocarbon (TPH) content is a combination of several hundreds hydrocarbons originating in crude oil, volatile petroleum hydrocarbons ranging from C-2 to C-5 (petrol range) and other extractable petroleum hydrocarbons ranging from C-6 to C-40 (diesel range). Since it is impractical to measure each of those components separately, the TPH measurement is used to assess the cumulative contamination of the crude oil in a spill. The TPH content of WAF may consider both the resolved and unresolved complex mixtures (UCM) including mixtures of branched and cyclic alkanes, naphthanoaromatics and also compounds with little polarity (Neff et al., 2000).

A complete list of the oil constituents recognized in WAF of oil is presented in Table 1-2.

Table 1-2: Oil constituents in WAF

Group		Target	Reference
Volatile Organic Compounds (VOC)	BTEX	Benzene	(Faksness et al., 2004; Hokstad et al., 2000)
		Toluene	
		Ethyl-benzene	
		Xylene (p,m,o-xylene)	
	Other saturates	2-Methylpentane	(Reddy et al., 2012; Daling, 2002; Faksness et al., 2008; Guadalupe and Gabardo 2002; Singer et al., 2000b; Brakstad et al., 2000; Malmquist et al., 2007; Grimmer and Jacob, 1983)
		2,4 Dimethylpentane	
		Isopentane	
		Hexane	
		Cyclopentane	
		Cyclohexane	
Volatile polar compound	Phenol	Phenol (C-1 to C-4)	
Semi Volatile organic compounds (SVOC)	Naphthalene	Naphthalene	
		Alkylnaphthalene (C-1 to C-4)	
	PAH (2-3 rings)	Alkylphenanthrene (C-1 to C-4)	
		Alkylfluorene (C-1 to C-3)	
		Alkyldibenzothiophene	

		(C-1 to C-4)	
		Biphenyl	
		Anthracene	
		Alkylanthracene (C-1 to C-4)	
	PAH (4+ rings)	Pyrene	
		Alkylpyrene (C-1 to C-4)	
		Chrysene	
		Alkylchrysene (C-1 to C-4)	
		Fluoranthene	
		Perylene	
		1,2-benzanthracene	(Whitehouse 1984)
Isoprenoids		Pristane, phytane	(Wang and Fingas 1997)
Total Petroleum Hydrocarbon (TPH)		*n*-C_{10} to *n*-C_{36} with unresolved complex mixture (UCM)	(Faksness et al. 2008; Neff et al. 2000)
		n-C_{10} to *n*-C_{36} without UCM	

1.3. Oil weathering

The pour point of spilled oil determines the extent of initial oil spread. If the seawater temperature is lower than the pour point, waxes will solidify as tar balls or slick (Concawe, 1983; Sebastiao and Guedes, 1996). Denser oil will sink while lighter fractions remain on top. The small droplets, which are separated from the slick, become entrained into the water column. This is supported by wind, ocean waves, currents, gravitational forces and also the interfacial tensions between oil and water. Those forces allow oil spread, overcoming viscous forces. While a fraction of oil completely dissolves in the water column, a fraction will form colloidal particles in emulsion form (Sterling et al., 2003).

There are a number of oil weathering processes happen in offshore. Evaporation is the most significant phenomena that can remove up to 40% of light crude including BTEX and other volatilities, and 20% of heavy crude oil within first few days at 15 ^{o}C (Hokstad et al., 2000; Wang and Fingas, 1995). The evaporation rate is dependent on the fraction of light hydrocarbons present in the crude oil, oil temperature, slick thickness and surface area as well as environmental conditions such as sea roughness and wind speed (Sebastiao and Soares, 1995). In cold environments, the evaporation of volatile components will be inhibited due to low temperatures and encapsulation of oil in ice (Brandvik and Faksness, 2009). In the long term, photo oxidation and biological degradation play a critical role in oil weathering process. Photo oxidation photo-chemically converts the surface oil components into acidic and phenolic compounds (Kiruri et al., 2013). Limited day light and ice cover slow down the photo oxidation

during winter periods. Water soluble oil components are readily converted to small organic compounds at fully oxidized to inorganic carbons by pelagic microorganisms in seawater from their anaerobic digestion. (Wang and Fingas, 1997; Radović et al., 2012). As temperature goes down, the rate of biodegradation also decreases making the natural remediation process slow (Jn et al., 1973). Figure 1-1 illustrates an overall weathering process that typically happens in the ocean.

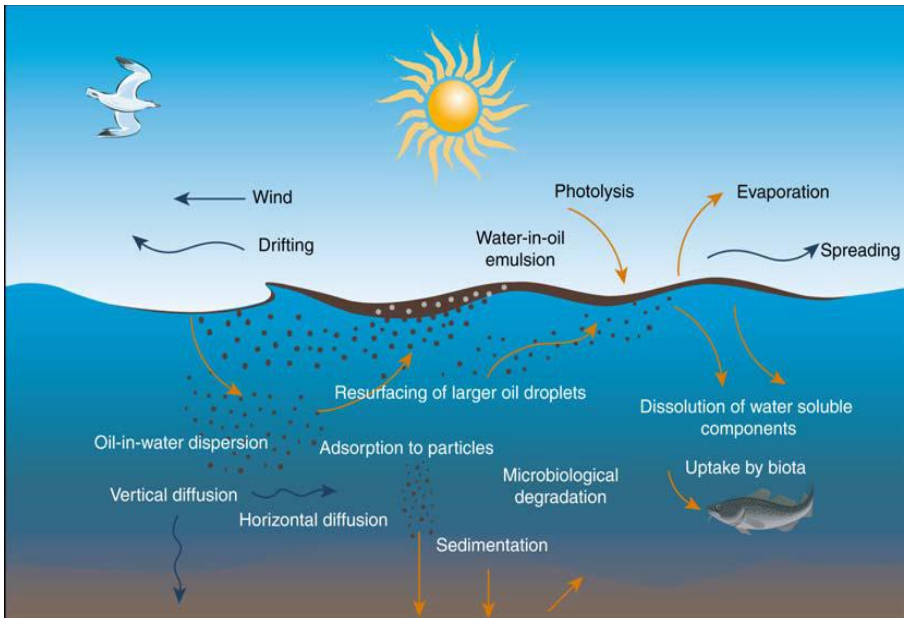


Figure 1-1: The weathering process in the ocean (Daling, 2011)

The toxicity of WAF of oil is reduced in weathered oil due to the loss of volatile components (predominantly BTEX). The heavier, relatively non-volatile and less water soluble components like PAHs (more than three rings) and polar/unresolved complex mixture (UCM) are still problematic with respect to environmental impacts (Hokstad et al., 2000). PAHs with higher number of rings and degree of alkylation are more resistant

to natural weathering than that of smaller and lesser alkylated PAHs (Yim et al., 2011). Yim et al. (2011) identified a higher percentage of C-2 and C-3 dibenzothiophenes and alkylated chrysenes in oil compared to naphthalenes, fluorenes and phenanthrenes as the oil weathered. The partitioning of these compounds between crude oil and seawater is typically described in terms of solubility or equilibrium concentrations.

1.4. Water solubilities and partition coefficients of oil components

The ratio between the concentrations of a substance in an organic liquid phase (C_l) to the water phase (C_w) of an immiscible system at equilibrium state is called the partitioning coefficient (K_{lw}), which is temperature specific:

$$K_{lw} = \frac{C_l}{C_w} \quad (1\text{-}1)$$

Since the fluids considered here are highly non-ideal, Raoult's law is not appropriate to calculate the equilibrium oil concentrations in water phase. As such, software packages such as HSC Chemistry, OLI Analyzer and Aspen are recommended to calculate the solubilities and compare to the experimental data. The following maximum solubility curves shown in Figures 1-2 and 1-3 were drawn using OLI Analyzer software package for some of the key oil analytes as a function of temperature in seawater at 35 ppt (parts per thousand) salinity at 1 atm pressure. OLI Analyzer used Helgeson-Kirkham-Flowers (HKF) equation of state for the simulation.

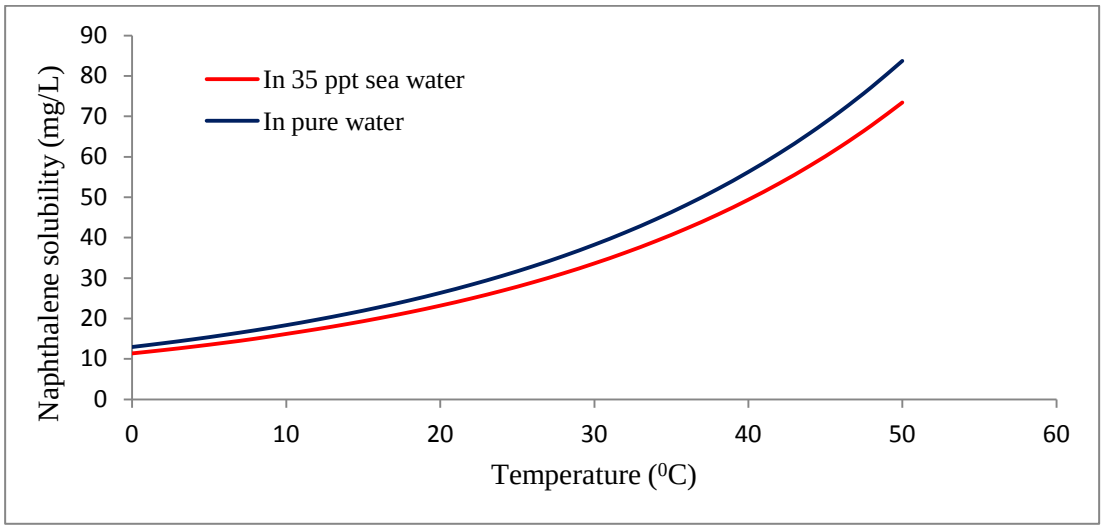


Figure 1-2: Equilibrium water solubility of naphthalene as a function of temperature in seawater (35 ppt salinity) and pure water

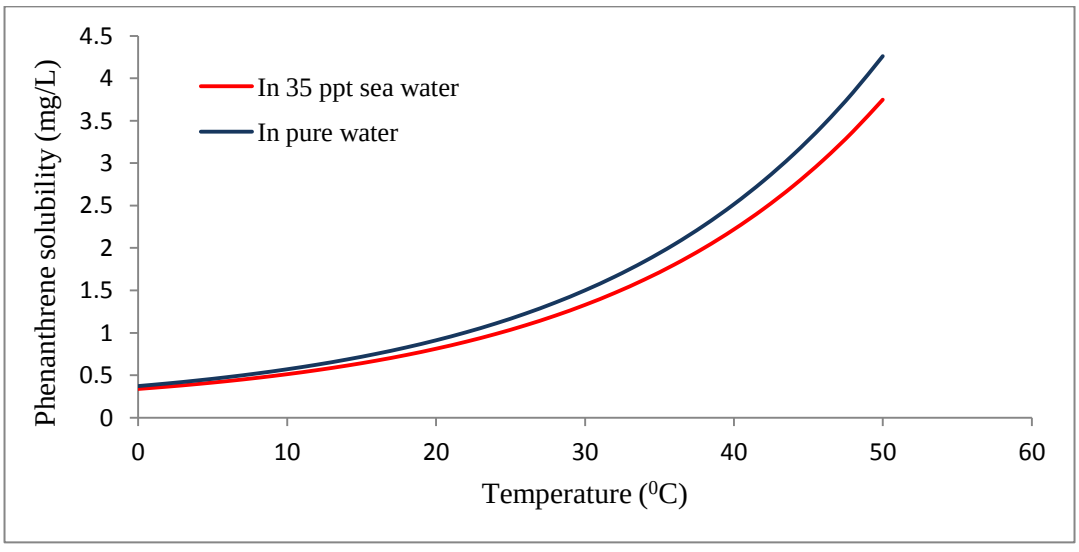


Figure 1-3: Equilibrium water solubility of naphthalene and phenanthrene as a function of temperature in seawater (35 ppt salinity) and pure water

According to Figure 1-2 and Figure 1-3, solubilities of both naphthalene and phenenathrene increase with temperature. There is a small salting-out effect at higher temperatures as shown by the two plots. Faksness et al. (2008) indicated BTEX and PAHs are subjected to the "salting out" effect reducing solubility in the seawater compared to fresh water due to the increased salinity.

1.4.1. Octanol-water partition coefficient

The octanol-water partition coefficient (K_{OW}) is a standard physicochemical measurement that calculates the ratio of the concentrations of a solute in immiscible octanol and water phases at equilibrium (Sangster, 1997). N-octanol can accommodate most of the typical solutes due to the dual nature of the compound, an apolar hydrocarbon group and a bipolar alcohol functional group. The K_{OW} of petroleum compounds is a good indicator of the solute's relative lipophilicity or hydrophobicity (Schwarzenbach et al., 2003). Table 1-3 summarizes K_{OW} values of some PAHs with their water solubility values.

Table 1-3: Water solubility and K_{OW} values for some PAHs at 25 ^{o}C and 1 atm, modified from (Sverdrup et al., 2002), if not stated otherwise

PAH	Molecular weight (g/mol)	Water solubility (µg/L)	log K_{OW}
Naphthalene	128.2	31700	3.32
Acenaphthylene	152.2	3930	4.07
Acenaphthene	154.2	16100	3.94
Fluorene	166.2	1980	4.23
Anthracene	178.2	73	4.50
Phenanthrene	178.2	1290	4.57[a]
Pyrene	202.2	135	5.20
Fluoranthene	202.2	260	5.20
Chrysene	228.3	2.0	5.80
Perylene	252.3	0.4	6.40
Phenol	94.11	-	1.15[b]

[a] (Ma et al., 2010)

[b] (Berthod and Carda-Broch, 2004)

Phenol has the lowest n-octanol-water partition coefficient among other oil components. Naphthalene is the secondly most water soluble component and the most soluble PAH among the list in Table 1-3.

PAHs are generally considered as large apolar or weakly mono-polar compounds (Berthod and Carda-Broch, 2004). In general, they do not readily partition to the water phase from an organic phase resulting larger activity coefficient values. As the number of benzene rings increases the partitioning coefficients show a gradual increase and subsequently lower levels of larger PAHs in water phase.

1.5. Oil behaviour in seawater

While the octanol-water partition coefficient is a useful indicator, it does not consider the complex matrix of petroleum and the subsequent impact on partitioning. As previously indicated, about 20% to 30% of the spilled oil disperses and/or dissolves into the upper water column within several days of the spill (Neff and Stubblefield, 1995). Sterling et al. (2003) found the solubilities of PAHs in a crude oil - saline water (30 ppt) system as shown in Table 1-4. The table compares those values with corresponding pure species solubilities found at 25 ^{o}C and 1 atm.

Small PAHs such as naphthalene and biphenyl with two benzene rings were more soluble in both pure water and seawater at room temperature. The solubility of naphthalene in seawater was almost similar to its water solubility as a pure species. The water solubilities of larger PAHs were smaller than that of smaller PAHs. Three ringed PAHs such as anthracene and phenanthrene were lesser soluble in seawater compared to naphthalene. The largest PAH; pyrene indicated even lesser solubility in seawater (from crude oil) compared to its water solubility as a pure species.

Table 1-4: [a]Solubilities of different PAHs in seawater at 30 ppt salinity at room temperature, modified from (Sterling et al., 2003) and [b]pure species solubility at 25 ^{o}C and 1 atm, modified from (Sverdrup et al., 2002)

PAH	Seawater solubility from crude oil (mg/L)[a]	Pure species solubility (mg/L)[b]
Naphthalene	31.75	31.70
Biphenyl	7.51	-
Acenaphthene	3.47	3.93
Fluorene	1.97	1.98
Dibenzothiophene	1.03	-
Anthracene	0.075	0.073
Phenanthrene	1.07	1.29
Pyrene	0.0001	0.135

Temperature increases the oil solubility in water (Faksness et al., 2008; Anderson et al., 1974; Gearing and Gearing, 1982). A 25 ^{o}C temperature drop can result a four-fold decrease in oil solubility in water (AMAP, 2010). Whitehouse (1984) studied the aqueous solubility of six PAHs by injecting water and pure PAH species in to a dynamic coupled column liquid chromatography (DCCLC) system. Figure 1-4 shows the trends of water solubility of PAHs with temperature within the salinity range from 0 to 36.7 ppt. According to that, the water solubility of phenanthrene, anthracene, 2-methylanthracene, 2-ethylanthracene, 1,2-benzanthracene and benzo(a)pyrene increased with temperature.

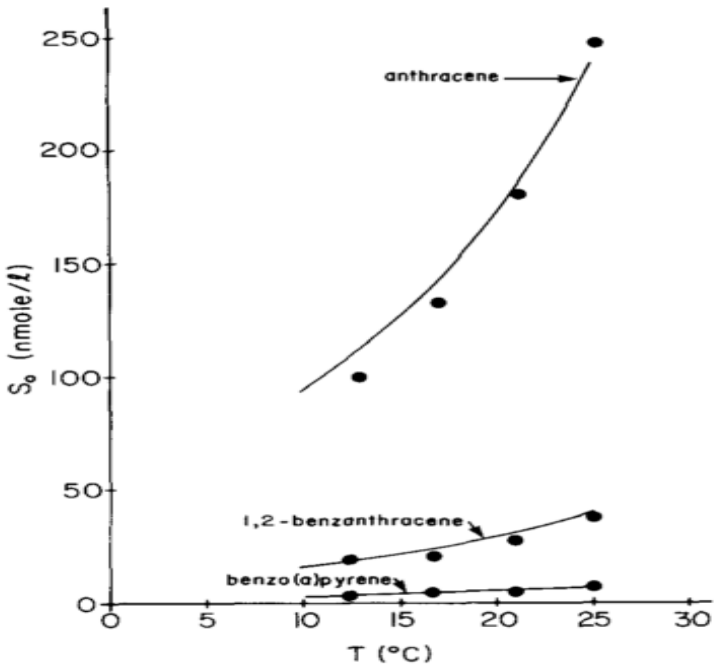


Figure 1-4: Solubility change of anthracene, 1,2-benzanthracene and benzo(a)pyrene in water as the system temperature increased from 3.7 ^{o}C to 25.3 ^{o}C (Whitehouse, 1984)

The effect of temperature on aqueous solubility is more significant for large, polar compounds such as PAHs (Schwarzenbach et al., 2003). Bennett and Larter (1997b) determined partition coefficients of alkylephenols were reduced as the temperature increased from 25 ^{o}C to 80 ^{o}C in an oil-seawater system due to the enhanced water solubility of alkylphenols. Perkins et al. (2005) did a WAF experiment by mixing crude oil in filtered seawater in aspiratory bottles. They found that the solubility of BTEX in seawater decreased as temperature increased from 7 ^{o}C to 25 ^{o}C. At 7 ^{o}C, BTEX accounted 94% of the total volatile organic compounds studied and it was 84% at 25 ^{o}C.

A solubility study done using pure alkylated benzene and water in a clamp-type optical cell by Sawamura et al. (2001) indicated a decrease of solubilities of toluene and ethylbenzene in water as the temperature increases from 0 to 20 ^{o}C. A minimum solubility occurred at 20 ^{o}C as illustrated in Figure 1-5.

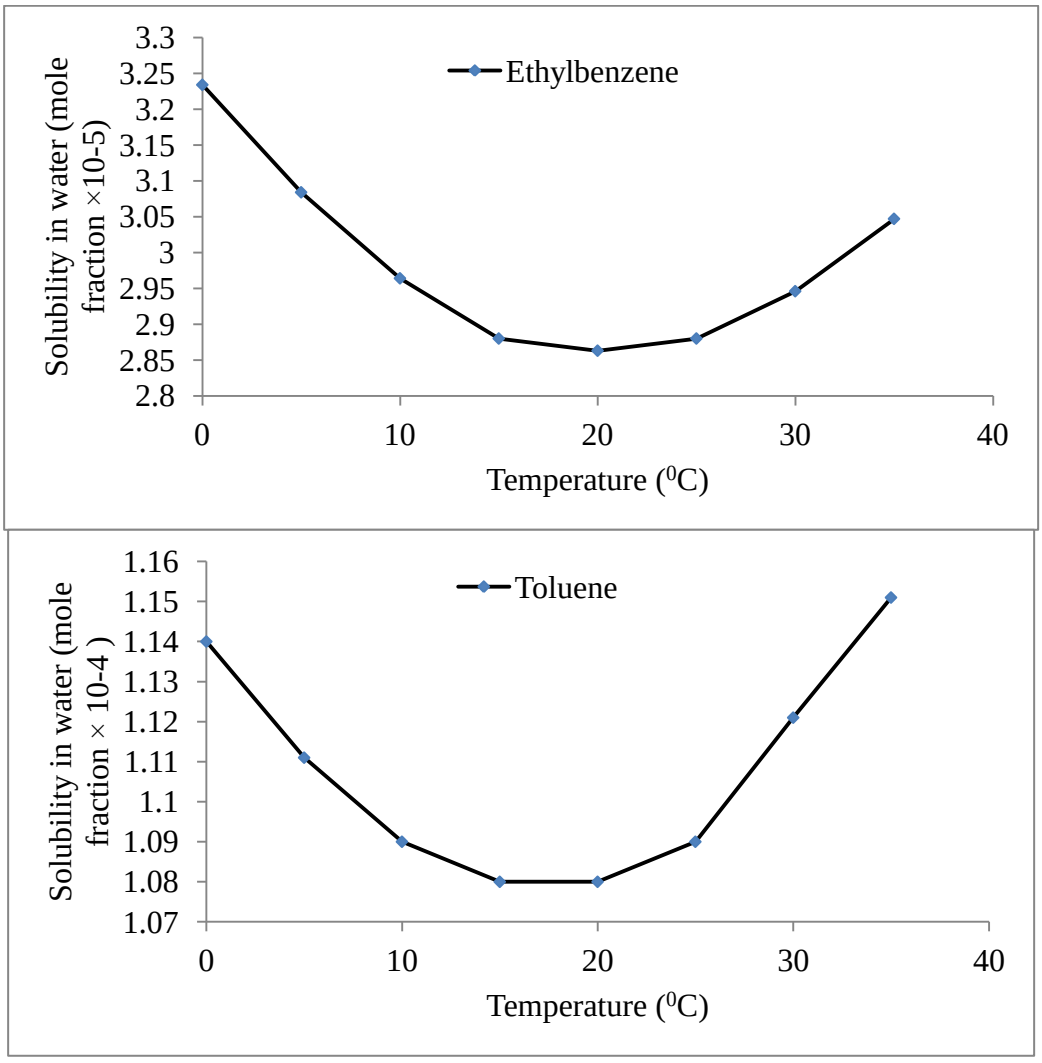


Figure 1-5 :Solubility of VOCs with temperature at 0.1 MPa pressure, modified from (Sawamura et al., 2001)

The partition coefficient can be expressed as a function of temperature by incorporating enthalpy and entropy changes by the Van't Hoff equation (Schwarzenbach et al., 2003).

$$\text{Log } (K_{OW}) = \frac{\Delta H}{R} \times \frac{1}{T} + \frac{\Delta S}{R} \quad (1\text{-}2)$$

Where,

ΔH : Enthalpy of fusion

ΔS : Entropy of fusion

R: Universal gas constant = 8.314 $JK^{-1}mol^{-1}$

T: Temperature in Kelvin

The above equation can be used to compare two K_{ow} values at two different temperatures.

$$\text{Log } (Kow_1) = \frac{\Delta H}{R} \times \frac{1}{T_1} + \frac{\Delta S}{R} \quad (1\text{-}3)$$

$$\text{Log } (Kow_2) = \frac{\Delta H}{R} \times \frac{1}{T_2} + \frac{\Delta S}{R} \quad (1\text{-}4)$$

By subtracting (3) - (4)

$$\text{Log } \left(\frac{K_{ow1}}{K_{ow2}}\right) = \frac{\Delta H}{R} \times \left(\frac{1}{T_1} - \frac{1}{T_2}\right) \quad (1\text{-}5)$$

From equation 1-5, the log (Kow) value of any compound can be calculated at temperatures relative to the standard value available at 25 ^{o}C.

Assumption: ΔH and ΔS values are assumed constant over the temperature range.

(ΔH and ΔS can be assumed to be constant over small temperature range (Schwarzenbach et al., 2003).)

Table 1-5: Enthalpy of fusion

Component	ΔH (KJ/mol)	Temperature of fusion (K)	Reference
Naphthalene	19.06	353.4	(Roux et al., 2008)
Fluorene	19.58	387.9	
Phenanthrene	16.46	372.4	
Pyrene	17.36	423.8	
Chrysene	26.2	531.4	
Phenol	11.51	314	(Bret-Dibat and Lichanot, 1989)

Figure 1-6 shows the calculated octanol-water partition coefficients for selected oil components as a function of temperature. Equation 1-5 was used to do the calculations.

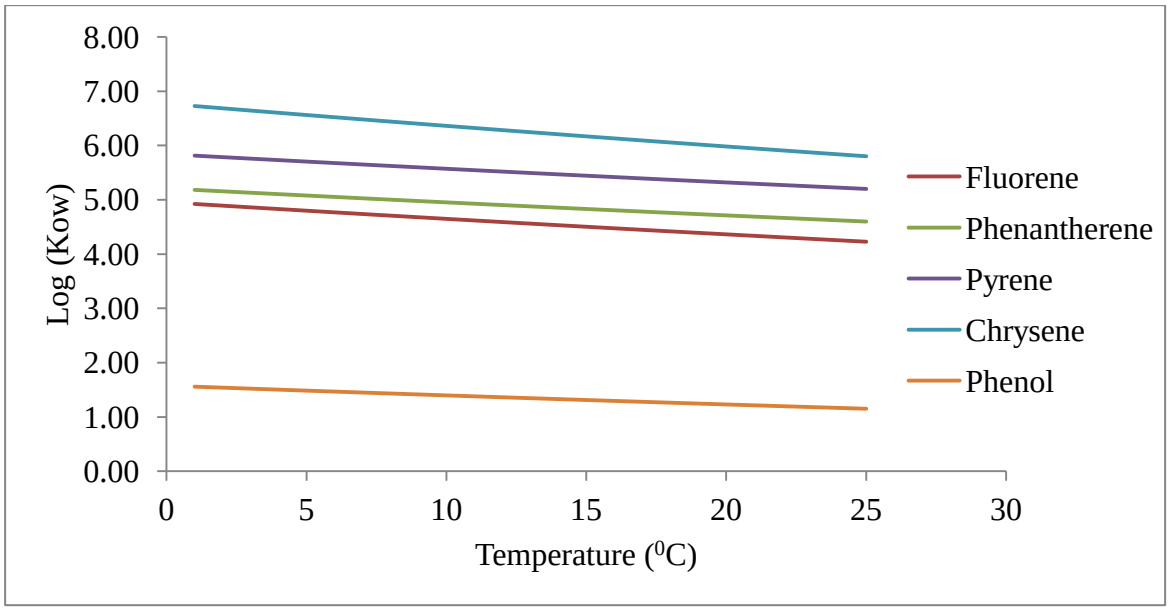


Figure 1-6: Calculated octanol-water partition coefficients as a function of temperature

The salinity of seawater also impacts solubility. The saturated concentration of a solute in a saline aqueous phase ($C_{w,salt}^{sat}$) can be found as:

$$C_{w,salt}^{sat} = C_w^{sat} \times 10^{-K[salt]} \quad (1\text{-}6)$$

Similarly, the resultant partitioning coefficient ($K_{ow,\ salt}$) can be found as:

$$K_{ow,\ salt} = K_{ow} \times 10^{+K'[salt]} \quad (1\text{-}7)$$

where, [salt] is the salinity of seawater (mol/L), C_w^{sat} is the saturated solute concentration in pure water, K' is is Setschenow constant or salting constant (unit M^{-1}) (Schwarzenbach et al., 2003).

Therefore Log ($K_{ow,\ salt}$) = Log (K_{ow}) + K'[salt] (1-8)

Table 1-6: Setschenow constant (K') (L/mol)

Component	Setschenow constant (K') (L/mol)	Reference
Naphthalene	0.28	(Schwarzenbach et al., 2003)
Fluorene	0.27	
Phenanthrene	0.3	
Pyrene	0.3	
Chrysene	0.34	
Phenol	0.13	

The octanol/water partition coefficients are calculated as a function of salinity and plotted in Figure 1-7.

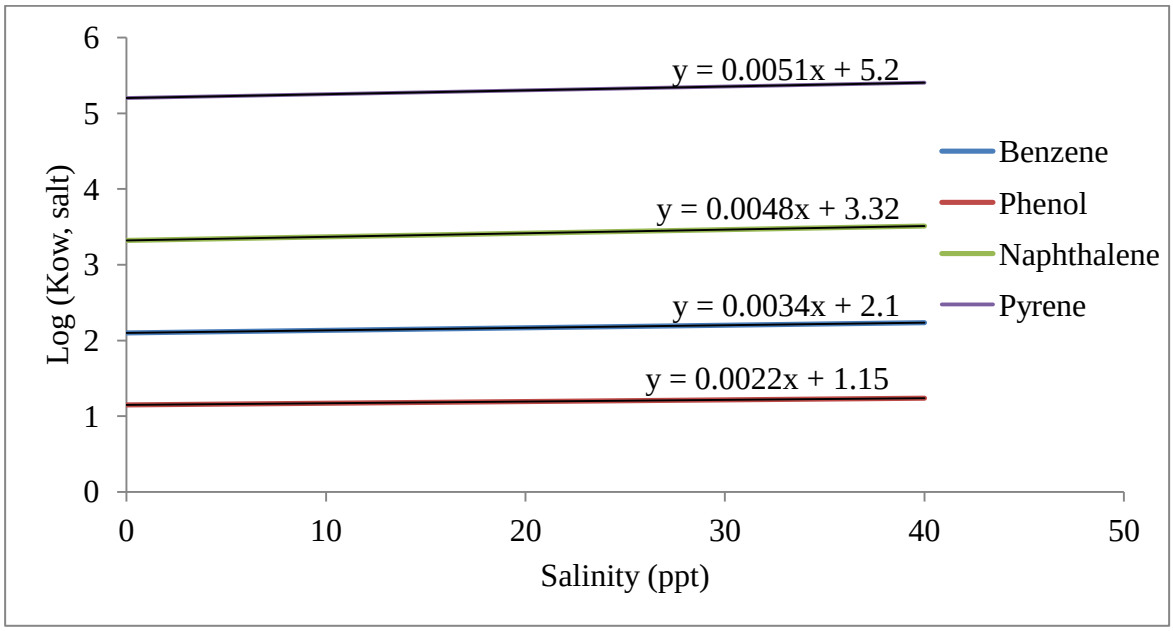


Figure 1-7: Octanol-water partition coefficients as a function of salinity at 25 ^{o}C

According to Figure 1-7, the partition coefficients of each of the four oil components increased as a function of salinity. This phenomena is commonly referred as "salting out" effect which depends on the nature of the component and the type of ions available in the seawater. As small gradients indicate all the above partition coefficients are weak functions of salinity.

Table 1-7 summarizes the solubility data collected by Shukla et al. (2007) which shows a decrease of solubilities of PAHs as the water salinity goes up from 0 ppt to 30 ppt. In their experiment, they used a 1:9 mixture of oil and water at 18 ^{o}C that was mixed 18 hours and allowed to settle 1 hour after mixing. Reitsma et al. (2013) in their WAF study noticed a slow partitioning of PAHs to from crude oil to water at low temperature and high salinity.

Table 1-7: PAH concentration of seawater at 1 ppt, 15 ppt and 30 ppt salinities prepared using artificial sea salt (Shukla et al., 2007)

PAHs	Concentration in water phase (ppm)		
	Salinity = 1ppt	Salinity = 15 ppt	Salinity = 30 ppt
Naphthalene	19.9	14.9	11.2
Phenanthrene	0.8	0.6	0.5
Fluorene	1.4	1.26	1.18
Pyrene	0.5	0.42	0.36
Chrysene	0.46	0.40	0.0

In the aforementioned study of water and pure PAH species in a DCCLC system by Whitehouse (1984) there was no significant solubility change for PAHs as salinity increased from 33 ppt to 36 ppt. He suggested that much of small salinity changes do not cause significant solubility changes of PAHs in water. However, he found a significant solubility drop of these constituents as temperature decreased from 25.3 ^{o}C to 4.6 ^{o}C all over the salinity range from 0 to 36.5%. He concluded as solubility of PAHs are more sensitive to temperature than salinity.

The octanol-water partition coefficients presented in Figure 1-6 were further corrected for 35 ppt (0.5989 mol/L, molar mass of NaCl = 58.44 g/mol) salinity using equation 1-8 and presented in Table 1-8.

Table 1-8: Corrected partition coefficients for salinity of 35 ppt

Temperature (^oC)	Log ($K_{OW, salt}$)					
	Naphthalene	Fluorene	Phenantherene	Pyrene	Chrysene	Phenol
1	4.16	5.08	5.36	5.99	6.93	1.63
5	4.04	4.96	5.26	5.88	6.76	1.56
10	3.90	4.81	5.13	5.75	6.56	1.47
15	3.75	4.67	5.01	5.62	6.37	1.39
20	3.62	4.53	4.89	5.50	6.18	1.31
25	3.49	4.39	4.78	5.38	6.00	1.23

The oil loading rate impacts the oil composition in the water phase. Hokstad et al. (1999) found 25 g/L spill of oil is a saturated system for Statfjord and Troll fresh crude oils in seawater. Couillard et al. (2005) studied the effect of oil loading in a chemical dispersant treated oil-water system. They noted a concentration increase of large PAHs from 9% to 20% in seawater at 30 ppt salinity as oil loading increased from 0.05 g/L to 2 g/L. However, they noted a drop of the initial naphthalene concentration from 86% to 70% in the water phase as oil loading increased. Sterling et al. (2003) observed a significant increase of TPH concentration from 1 ppm to 100 ppm in WAF as oil loading increased from 1 mL to 10 mL in 20 mL of simulated seawater at 30 ppt salinity.

Table 1-9 summarizes the effects of different factors on oil solubility and partitioning of BTEX and PAHs.

Table 1-9: Effects of different factors on oil solubility of WAF

Factor	Effects on	
	BTEX	PAHs
Temperature	- Approximately 10% decrease of concentration of toluene and ethylbenzene in water phase as temperature increased from 0 - 20 ^{o}C (Sawamura et al., 2001).	- Water solubility of 6 PAHs increased as temperature increased from 3.7 ^{o}C to 25.3 ^{o}C in a DCCLC system (Whitehouse, 1984).
Time	- A decrease of concentration in WAF as mixing time increased from 48 to 60 hours (leakage effected results) (Faksness et al., 2008).	- Mixing time needed for the WAF equilibrium was 24 hours in the range of 1 - 10 g/L oil loading at room temperature (Singer et al., 2000) - More than 48 hours needed to reach saturate conditions in WAF at lower temperatures around 2 ^{o}C (Faksness et al., 2008).
Seawater salinity		- Increased oil/water partition coefficients of alkylephenols as the salinity increased from 0 to 10 ppt (Bennett and Larter, 1997) -Decrease of water solubility of PAHs

		as water salinity increased 0 to 30 ppt (Shukla et al., 2007). - Small salting out effect from 33 ppt to 36 ppt salinity range in water and pure PAH species system (Whitehouse, 1984). - Slower equilibration of PAHs was found at higher salinities (up to 36.7 ppt) and lower temperatures (2 ^{o}C) in a study of WAF the polyethylene passive sample technique (Reitsma et al., 2013).
Oil loading		- Concentration of large PAHs increased from 9% to 20% in seawater at 30 ppt salinity as oil loading increased from 0.05 g/L to 2 g/L. Also noted a drop of the initial naphthalene concentration from 86% to 70% in the water phase (Couillard et al., 2005). - The concentrations of PAHs in WAF increased from 0.07 to 10.08 ppm as oil loading increased from 10 mg/L to

		10 g/L (Hokstad and Daling, 1999)
Chemical dispersant		- Increased Naphthalene concentration in CEWAF compared to WAF at 18 ^{o}C (Ramachandran et al., 2004). -A greater than 10 fold increase of PAH concentration in CEWAF compared to WAF in a 150 L glass aquaria with seawater in 4 ppt 18 ppt salinity range (Kuhl et al., 2013).

1.6. Chemically dispersed oil

Chemical dispersants are applied on the surface oil slick as a mitigation technique to reduce the risk of near-shore and coastal surface contamination by spilled oil. Dispersants are preferred over mechanical recovery methods in high energy sea conditions, as at those conditions effectiveness of mechanical methods can be reduced by 10 to 20% (Fiocco and Lewis, 1999). Chemical dispersant consists of surface active agents called surfactants with the ability of binding both water and oil from their hydrophilic and lipophilic ends respectively. Dispersants reduce the oil-water interfacial forces to form small oil-surfactant micelles, dispersing oil into the water column without forming a surface slick (Kuhl et al., 2013; Ramachandran et al., 2004). Figure 1-8 is an illustration of the mechanism of chemical dispersants.

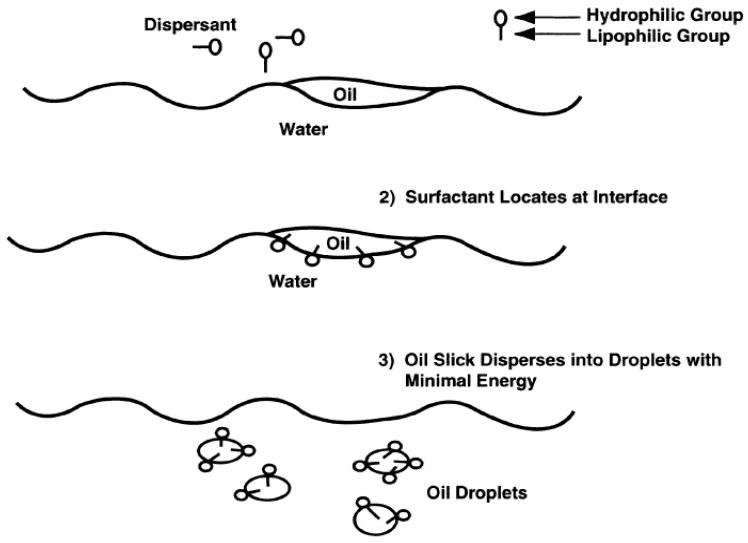


Figure 1-8: Mechanism of chemical dispersants (Lessard and DeMarco, 2000)

The effectiveness of the dispersant depends on the composition of the oil and dispersant, dispersant to oil ratio, the method of application and importantly the mixing energy of oil-water and dispersant in the system. In high energy oceans such as North Atlantic, the high mixing energy promotes the oil dispersion into the water column. However, the composition, viscosity and the thickness of the oil slick impact the effectiveness of the chemical dispersant (Fiocco and Lewis, 1999). According to a number of studies, the chemical dispersion can result in short term acute toxicity to pelagic organism as it increases the oil concentration (specially those of low molecular weight hydrocarbons) in water column (Wolfe et al., 2001). The oil is principally available in the form of colloidal micelles rather than in truly dissolved form (Fuller et al., 2004). Kuhl et al. (2013) showed that addition of chemical dispersant generally causes more than 10 fold increase of PAHs in WAF for an oil spill in the range of 4 to 18

ppt salinity (in 16.4 ^{o}C to 21.1 ^{o}C temperature range). However, weathering caused reduction of PAH concentration with the time as shown in Figure 1-9.

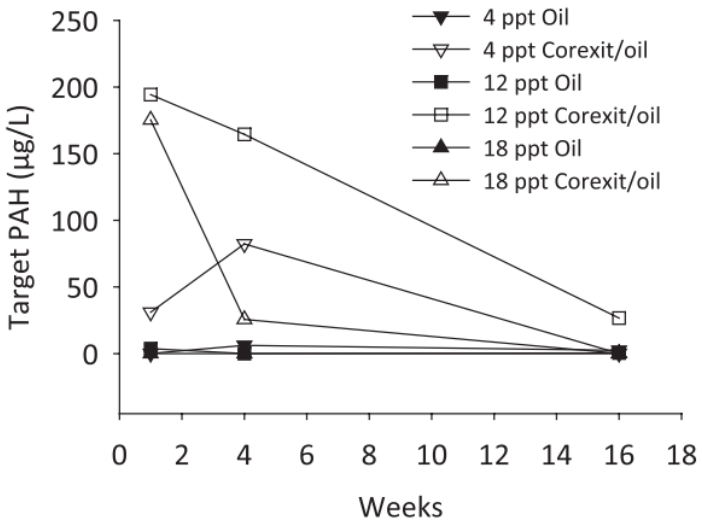


Figure 1-9: Effect of chemical dispersants (COREXIT 9500) on PAH concentrations in water phase with time at 4, 12 and 18 ppt salinities in a 150 L glass aquaria (Kuhl et al., 2013)

Ramachandran et al. (2004) did a WAF study by mixing crude and water in a 1:9 ratio at 18 ^{o}C. They secondly treated the WAF with chemical dispersants which were added at a ratio of 1:20 dispersant:oil at the same conditions. They found that the concentration of methylphenanthrene was two to four times higher in CEWAF than WAF. The concentration of dimethyldibenzothiophene was five to 10 times higher. Further, the study indicated that the difference in oil concentration in CEWAF is dependent on the viscosity of oil. Couillard et al., (2005) found that the concentration of

alkyl homologues, naphthalenes, 1 to 4 dibenzothiophenes and 1 to 4 phenanthrenes were increased in CEWAF compared to untreated oil. Chrysene and pyrene were identified only in CEWAF but not in WAF. Cohen and Nugegoda (2000) observed a six to seven times higher concentration of TPH in CEWAF compared to WAF in a WAF/CEWAF study done in a 20 L mixing chamber by mixing oil and seawater at 1:10 ratio and dispersant:oil at a 1:30 ratio at room temperature.

Salinity is one of the factors that causes reduced dispersant efficiency. Sutton et al., (1975) in their study identified a 68% reduction of the solubility of twelve aromatic hydrocarbons in seawater compared to fresh water both with chemical dispersant. This was again confirmed by Kuhl et al. (2013) in their CEWAF study.

1.7. Conclusions

This review gives an overall understanding about the previous work and findings about the behaviour of spilled oil in seawater under different conditions. Most of the published works on BTEX, PAHs and TPH were done at temperate conditions hence the knowledge in cold conditions is still limited. There is a gap of oil partitioning data in colder temperatures (from 2 to 25 ^{o}C), which is important to be filled. Previous studies identified that oil-water partitioning changes as a function of mixing time, temperature, water salinity and oil loading. Most of the studies examined one the effects of one or two of those factors on oil partitioning. One experiment that studies all the main factors together is worthwhile to have a better idea about the oil partitioning in to seawater.

Application of chemical dispersant is a widely used remediation technique particularly in high energetic oceans. Dispersants alter the partitioning pattern hence change the fate of oil in the ocean. Increased oil content predominantly in the form of emulsion droplets was found in most of the CEWAF studies that resulted higher initial toxicity to marine animals.

1.8. Objectives of the study

The objective of this study is to examine the oil-water partitioning bahaviour of selected PAHs, benzene and alkanes (as TPH) at cold seawater conditions. The key factors identified by reviewing the literature such as mixing time, temperature, oil loading and application of chemical dispersants are studied to find the influences of those on oil partitioning. The information could be used in future oil spill fate identification and remediation purposes.

2. Crude Oil Analysis

2.1 Introduction

Crude oil is the main petroleum product extracted from the earth and is composed of a number of hydrocarbons ranging from light hydrocarbons to heavier asphaltenes and waxes, as well as organic and inorganic sulfur, nitrogen and trace metals (Wang and Fingas, 1997). Physical properties of crude oil such as density and viscosity (Chen et al., 1974), oil-ice interfacial forces (Kawamura et al., 1986), pour point (González et al., 2006) among others determine the way oil behaves in water. Types of oil constituents and their concentrations in water depend on the source and type of the oil spilled (Wang and Fingas, 1997).

Crude oil collected from Newfoundland offshore oil production fields was used in this study. Before carrying out the oil-seawater partitioning studies, some of the basic physical properties of crude oil were measured to gain an understanding of the type of crude oil. The colour, density and viscosity are some of the most common physical properties that are useful in classifying crude oil. This study measured all of them and calculated the API gravity of the crude oil based on the specific gravity. The oil was analyzed to identify and quantify the target oil components. The targeted components were monocyclic and polycyclic aromatic hydrocarbons that have been identified as important oil constituents in terms of environmental pollution in offshore oil spills (Aas et al., 2000; Bennett and Larter, 1997; Faksness et al., 2008; Yan et al., 2004). Naphthalene was selected as a PAH with two benzene rings. Phenanthrene and fluorene which represent three ringed PAHs were analyzed along with dibenzothiophene which is

also a PAH with three heterogeneous rings with sulphur. Pyrene and chrysene were selected as large PAHs with 4+ rings. Additionally, phenol, a volatile polar compound, was analyzed along with three of the selected alkylated phenols. Alkanes were also analyzed as TPH (Neff et al., 2000). Gas chromatography-mass spectrometry technique was used in the chemical analysis.

2.2 Materials and Methods

2.2.1 Crude oil sampling

Crude oil was collected and brought from the production field according to the following procedure (Modified from ASTM D4489-95 (ASTM, 2014); ASTM D3325-90 (ASTM, 2014a)).

- Pre-cleaned 1 L amber glass bottles with PTFE lined screw caps and coolers were sent to the offshore production platform.
- Crude oil was filled up to the top of the amber bottles allowing a minimal head space with air and closed tightly with the caps.
- Bottles were stored in the cooler filled with ice at approximately 4 ^{o}C / 5 ^{o}C temperature and transported to the lab within 24 hours.
- They were stored in a refrigerator at < 2 ^{o}C.

The samples were not acidified, as is typical in sampling procedures for petroleum. Acidification impacts partitioning behaviour and may have other impacts that would affect the partitioning experiments. However, acidification is usually used to halt

microbial activity (i.e. biodegradation of petroleum). Although keeping the samples below 4 ^{o}C should mitigate microbial activity, in order to be certain there was minimal biodegradation, a reference sample was taken for analysis.

At the time of sampling, a 100 mL crude oil sample was acidified to a pH of 2 by adding concentrated hydrochloric acid (HCl). This sample will be referred to as "reference sample" in the next sections of this document. The purpose of collecting this sample was to determine if there was any sample biodegradation during transport. By acidifying this sample, the degree of biodegradation during transport can be assessed through a comparison of reference and "non-preserved" sample analysis.

2.2.2 Density analysis

A 10 mL glass pycnometer was weighed with its glass stopper then filled to the top with crude oil and closed with the stopper. The total weight was measured using a laboratory balance as shown in Figure 2-1 at room temperature. From the difference between the two weights, the weight of crude oil in the pycnometer was calculated and density was calculated.

Figure 2-1: Weighing the filled pycnometer

2.2.3 Viscosity analysis

The viscosity of the crude oil was measured using BROOKFIELD DV-III ULTRA Programmable Rheometer as shown in Figure 2-2. The rheometer was leveled on an even table surface using its adjustable legs. The heater and cooler were turned on and then the flowing water temperature was set to 30 ^{o}C. The sample container was filled with approximately 7 mL of crude oil and fixed to the rheometer. A spindle of size 18 was fixed to the rotary shaft and immersed in oil. The motor was turned on after that. The rotational speed of the spindle was increased gradually so that it gave a maximum torque (the higher the torque, the better the reading). Finally, the viscosity was recorded at the steady state. The specifications used for the measurement are presented in Table 2-1.

Figure 2-2: Viscosity measurement by the programmable rheometer

Table 2-1: Specifications of the rheometer

Setting	Level
Temperature	30 ^{o}C (Actual reading of the sample was 29.7 ^{o}C)
Max. rotational speed	250 rpm
Max. torque	64.8 %
Shear stress	25.6 D/cm^{2}
Shear rate	330 s^{-1}

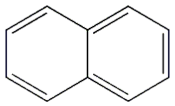
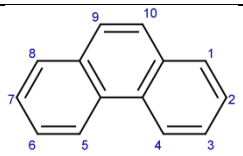
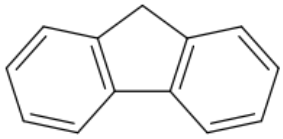
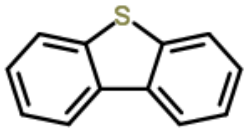
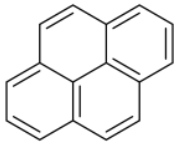
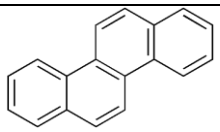
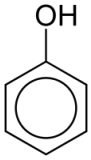
2.2.4 Analysis of oil constituents

After reviewing the literature on components of oil and contaminants of concern, six of the main PAHs, which represent different groups of PAHs, were selected to be studied (Table 2-2). Naphthalene, which has two benzene rings, is the smallest PAH in the list. It has the smallest boiling point and is the most volatile PAH compared to the other five of them. Three ring PAHs include fluorene, phenanthrene and dibenzothiophene. The largest PAHs with four benzene rings and higher boiling points include pyrene and chrysene.

Phenol and four of the alkylated phenols were also included in this list. The TPH concentration was measured as cumulative C8 to C34 alkane amount with the unresolved complex mixture (UCM).

A 1000 ppm crude oil sample was prepared by dissolving 100.00 mg of crude oil in 100 mL of GC-grade dichloromethane (DCM). The sample was spiked with the surrogate internal standard (IS), acenaphthene-d_{10}. An average response factor was calculated using the IS which was used to adjust the final concentrations of analytes. All the oil analyses of this study were performed by gas chromatography-mass spectrometry (GC-MS).

Table 2-2: Target analytes and properties

Category	Oil component	Boiling point (^{o}C)	Molecular structure
PAH (2 rings)	Naphthalene	218	
PAH (3 rings)	Phenanthrene	340	
	Fluorene	295	
PAH (3 rings with functional groups)	Dibenzothiophene	332	
PAPAHs (4+ rings)	Pyrene	404	
	Chrysene	448	
Volatile polar compounds	Phenol	181.7	

2.2.5 Gas chromatography-mass spectrometry (GC-MS)

Common methods of crude oil analysis include gravimetric methods, high performance liquid chromatography (HPLC), infrared chromatography (IR), ultraviolet (UV) spectrometry and gas chromatography (Wang and Fingas, 1995). Gas chromatography-mass spectrometry (GC-MS) and GC with flame ionization detection (GC-FID) are two of the most extensively used techniques in current studies.

In this study a Network GC System 6890N with 7683 Series Injector and a 5973-Inert Mass Selective Detector from Agilent Technologies, ON, Canada, which were operated in C-CART laboratory in the Chemistry Department at Memorial University of Newfoundland, Canada were used. All the analyses were carried out using the GC-MS instrument.

The GC was used in splitless mode in all the analyses. Helium was the carrier gas. The GC column was a DB-5ms capillary column by Agilent (Model: Agilent 122-5532) with dimensions of 0.25 mm diameter, 30 m length and 0.25 μm film coating. More details about the instrument and method used to analyze each set of analytes can be found from the methods attached in the Appendix.

2.2.6 Stock solutions

A stock solution (SS) was prepared for each PAH, phenol and TPH using standard analytical materials bought from Sigma-Aldrich, Canada Co.

The stock solution of PAHs that was intended to be used for crude oil analysis contained the standards presented in Table 2-3 and for phenol and alkylated phenols in Table 2-4.

Table 2-3: Composition of the stock solution of PAHs

Standard material	Grade	Amount dissolved in 100 mL of DCM	Concentration in SS
Naphthalene	99%	10.0 mg	100.0 ppm
Acenaphthene-d_{10} (IS)	Analytical standard	10.0 mg	100.0 ppm
Fluorene	Analytical standard	5.0 mg	50.0 ppm
Dibenzothiophene	Analytical standard	5.0 mg	50.0 ppm
Phenanthrene	Analytical standard for environmental analysis	5.0 mg	50.0 ppm
Pyrene	Certified reference material	5.0 mg	50.0 ppm
Chrysene	Analytical standard	5.0 mg	50.0 ppm

Table 2-4: Composition of the stock solution of phenols

Standard material	Amount dissolved in 100 mL of DCM	Concentration in SS
phenol	10.00 mg	100.0 ppm
ortho-cresol	10.00 mg	100.0 ppm
meta-cresol	10.00 mg	100.0 ppm
4-Ehylphenol	10.00 mg	100.0 ppm

A standard TPH mixture containing C8 to C38 n-alkanes (2000 µg/mL in dichloromethane) from Sigma-Aldrich Canada Co. was used to prepare the 100 ppm TPH stock solution. A baseline integrated concentration of octane (C8), decane (C10), dodecane (C12), tetradecane (C14), hexadecane (C16), octadecane (C18), eicosane (C20), docosane (C22), tetracosane (C24), hexacosane (C26), octacosane (C28), triacontane (C30), dotriacontane (C32), tetratiocontane (C34), hexatriacontane (C36) and octatriacontane (C38) was considered with UCM in measuring TPH.

The standard sample preparation and extraction method EPA 3510 (Faksness and Brandvik, 2008), PAH analysis method EPA 8270D (Kuhl et al., 2013; Neff et al., 2000) and TPH analysis methods EPA 8015/ASTM 3328 (Wang and Fingas, 1997) and EPA 8100 (Faksness et al., 2008) were used as guidance in sample preparation and analysis. Stock solutions were run in GC-MS in full scan mode in which the whole span of masses were monitored (as mass to charge ratio indicated as m/z). The major qualitative and quantitative ion fragments (m/z) and retention times of those in the capillary column were noted from that first full scan run. The GC-MS was run in the selective ion monitoring (SIM) mode due to the low concentrations of target analytes in the samples. Separate GC methods were developed for PAHs, phenols and TPH in SIM mode from m/z values and corresponding retention times obtained from full scan runs. A full scan run was performed before each batch of runs to adjust the method for any changes that happened. The complete methods are attached in the Appendix.

2.2.7 Standard addition

The standard addition analytical technique was used to quantify the concentrations of each analyte by GC-MS. The following calculation was done to find an unknown concentration of a target anayte (x) according to the standard addition.

The peak area of the chromatogram for the analyte x is proportional to its concentration in the sample.

$$PA = P'C_T \quad (2\text{-}1)$$

where PA is the peak area of the chromatogram (response for anayte x), C_T is the resultant concentration of analyte x in the final sample and P' is a proportionate constant.

$$C_T = \frac{C_S V_S + C_x V_x}{V_T} \quad (2\text{-}2)$$

where C_s is the concentration of x in the SS, V_s is the volume of the SS, C_x is the concentration of x in the oil sample, V_x is the volume of the oil sample and V_T is the total volume of the final sample that is to be analyzed (SS + oil sample).

Therefore,

$$PA = P'\left(\frac{C_S V_S + C_x V_x}{V_T}\right) \quad (2\text{-}3)$$

The linear form of the above equation gives the following:

$$PA = \frac{P'C_S}{V_T} V_S + \frac{KC_x V_x}{V_T} \quad (2\text{-}4)$$

Four samples were prepared with different volumes of SS (V_s) as shown in Table 2-5. The peak areas (PA) obtained for each of the four samples were plotted against the

corresponding V_s. The unknown concentration C_x was found using gradient (m) and intercept (C) of the plot as follows.

$$\frac{C}{m} = \frac{C_x V_x}{C_s} \quad (2\text{-}5)$$

Therefore,

$$C_x = \frac{CC_s}{mV_x} \quad (2\text{-}6)$$

Table 2-5: Compositions of four samples prepared to determine the concentrations of target analytes in oil by the standard addition technique

Component	Sample # 1 (mL)	Sample # 2 (mL)	Sample # 3 (mL)	Sample # 4 (mL)
Volume of SS (V_s)	0	1	2	3
Volume of oil sample (V_x)	7	7	7	7
Make-up DCM volume	3	2	1	0
Total volume (V_T)	10	10	10	10

2.3 Results and discussion

2.3.1 Physical properties

Different crude oils have different physical properties such as colour, density and viscosity depending on origin and type (Radović et al., 2012). Therefore, an analysis of

physical properties is useful in identifying the type of the crude oil and the way it behaves in a spill.

The colour of the crude oil in this study was middle brown. The density was 0.8553 ± 0.0021 g/mL (mean ± SD) at room temperature (20 ^{o}C). The density of water (de-ionized) was 0.9976 ± 0.0019 g/mL at the same conditions. The specific gravity of crude oil was calculated using Equation 2-7 which was 0.8573 at room temperature.

$$\text{Specific Gravity (SG)} = \frac{\text{Density of crude}}{\text{Density of water}} \quad (2\text{-}7)$$

American Petroleum Institute gravity (API gravity) is the well known industrial measurement that was defined by the American Petroleum Institute to indicate densities. The API gravity of the crude oil was calculated as in Equation 2-8. It was 33.55 at room temperature.

$$\text{API gravity} = \frac{141.5}{\text{SG}} - 131.5 \quad (2\text{-}8)$$

where, SG is the specific gravity of oil.

API gravity ranges from 10-20 for heavy crude oils, 20-25 for medium crude oils and above 25 for light crude oils (Crude oil, 2015). The API gravity of the crude oil used in this study falls under the light crude oil category according to the above definition. West Texas intermediate (API 40), Canadian syn-crude (API 33) and Arab light (API 32) are some of the standard light crude oils (Bp, 2011). The crude oil used here is a Canadian syn-crude according to that categorization.

The dynamic viscosity of crude oil was 7.75 ± 0.02 centiPoise (cP) (mili Pascal Second (mPaS)) which is in the range of light crude oil (Ai-besharah et al., 1987; Bp, 2011).

Therefore, the crude oil used in this study can be considered a light crude oil with middle brown colour, high API gravity and low viscosity.

2.3.2 Oil composition

Concentrations of six PAHs were measured in the crude oil. These values are to be used in oil-seawater partitioning coefficient calculations in subsequent sections.

As mentioned earlier, a reference crude oil sample was preserved with HCl just after sampling to control any bio-degradation during the transportation to the laboratory. Concentrations of each of the target analytes was estimated in both non-preserved crude oil and reference crude oil. This was to compare and see if any significant loss occurred due to biodegradation during transportation. Table 2-6 shows the results obtained for those two crude oil samples. A two-sample t-test was done to find out any significant difference of analyte concentrations between those two at 95% confidence limit (α = 0.05).

Table 2-6: Concentrations of six PAHs and phenol in reference and non-preserved crude oil samples and the difference between them

Analyte	Reference crude oil		Non-preserved crude		P value of two-sample t-test (95% confidence interval)	Significant difference at $\alpha = 0.05$
	Conc. (ppm)	SD	Conc. (ppm)	SD		
Naphthalene	1127.67	11.63	1109.95	7.95	0.1260	No
Fluorene	292.00	3.58	278.82	3.21	0.2430	No
Dibenzothiophene	30.88	2.40	25.69	3.18	0.1090	No
Phenanthrene	452.30	17.37	454.23	23.06	0.9150	No
Pyrene	30.26	1.92	32.85	1.29	0.1245	No
Chrysene	54.56	4.56	57.19	6.13	0.5930	No
Phenol	321.54	11.27	316.55	16.02	0.6818	No

According to Table 2-6, no significant differences were identified in all the PAHs and phenol at 95% confidence interval. Therefore, the degradation during transportation can be considered to be insignificant.

According to the data, naphthalene dominates in crude oil, having 1109.67 ± 7.95 ppm in concentration. Other smaller PAHs such as fluorene and phenanthrene are more

available compared to those larger PAHs such as pyrene and phenanthrene, which is in agreement with what Faksness et al. (2008) found in their study. The phenol concentration was 316.55 ± 16.02 ppm.

The percentage errors of GC analysis associated with the above measurements in ppm range were calculated by running a standard sample of the same concentration range in the GC under the same conditions. Three replicates were used to estimate the uncertainties. The results are presented in Table 2-7.

Table 2-7: Errors associated with GC analysis of a standard sample of ppm range concentration

Analytes	Anticipated concentration in the standard (ppm)	Detected concentration by GC-MS (ppm)	% Error
Acenaphthene-d_{10} (IS)	10.20 ± 0.01	9.38 ± 0.54	8.04
Naphthalene	100.05 ± 0.01	94.37 ± 1.64	5.67
Fluorene	100.02 ± 0.01	93.76 ± 2.18	6.27
Dibenzothiophene	10.20 ± 0.02	8.69 ± 1.17	14.83
Phenanthrene	10.05 ± 0.01	9.14 ± 0.43	9.13
Chrysene	10.11 ± 0.01	9.04 ± 0.45	10.60
Pyrene	10.10 ± 0.01	8.97 ± 0.72	11.18
Phenol	10.01 ± 0.02	8.35 ± 2.49	16.58

The highest percentage detection error was reported for phenol which was 16.58% lower than the anticipated reading. Dibenzothiophene has a 14.83% reduction of the expected concentration, while it is 11.18% for pyrene. All the other analytes indicated errors less than 10% of the expected values.

Table 2-8 presents the concentrations of some PAHs in North Sea crude oil which were published by Aas et al. (2000). According to this data, the measured concentrations are within the range of the published values. Dibenzothiophene was not included in the study by Aas et al. (2000). The concentration of dibenzothiophene was measured as 25.69 ± 3.18 in this study.

Table 2-8: PAH concentrations in North Sea crude oil (Aas et al. 2000) and measured concentrations in this study

Component	Concentration in North sea crude oil (ppm) (Aas et al. 2000)	Measured concentration in non-preserved crude oil (ppm)
Naphthalene	1169	1109.95 ± 7.95
Fluorene	265	278.82 ± 3.21
Dibenzothiophene	Not Applicable	25.69 ± 3.18
Phenanthrene	238	454.23 ± 23.06
Pyrene	20	32.85 ± 1.29
Chrysene	26	57.19 ± 6.13

As an extension to phenol analysis, four more selected alkylated phenols were quantified in non-preserved crude oil: ortho-cresol (o-cresol), meta-cresol (m-cresol), para-cresol (p-cresol) and 4-ethylphenol. Due to a technical difficulty of separating the m and p cresols they were quantified together as a single group.

Table 2-9: Concentration of alkylated phenols in non-preserved crude oil

Alkylated phenol	Concentration (ppm)
o-Cresol	97.34 ± 4.98
m/p-cresol	77.04 ± 4.68
4-Ethylphenol	90.85 ± 6.05

According to Table 2-9, both o-cresol (97.34 ± 4.98) and 4-ethylphenol (90.85 ± 6.05) are in higher concentrations than the combined concentration of m-cresol and p-cresol (77.04 ± 4.68). The concentrations of those are lesser in crude oil compared to phenol.

TPH concentration as the baseline normalized total concentration of alkanes from octane (C8) to tetratriacontane (C34) with UCM was calculated in non-preserved crude oil. It was recorded as 1284.40 ± 13.87 ppm. The chromatogram obtained for TPH in crude oil is shown in Figure 2-3.

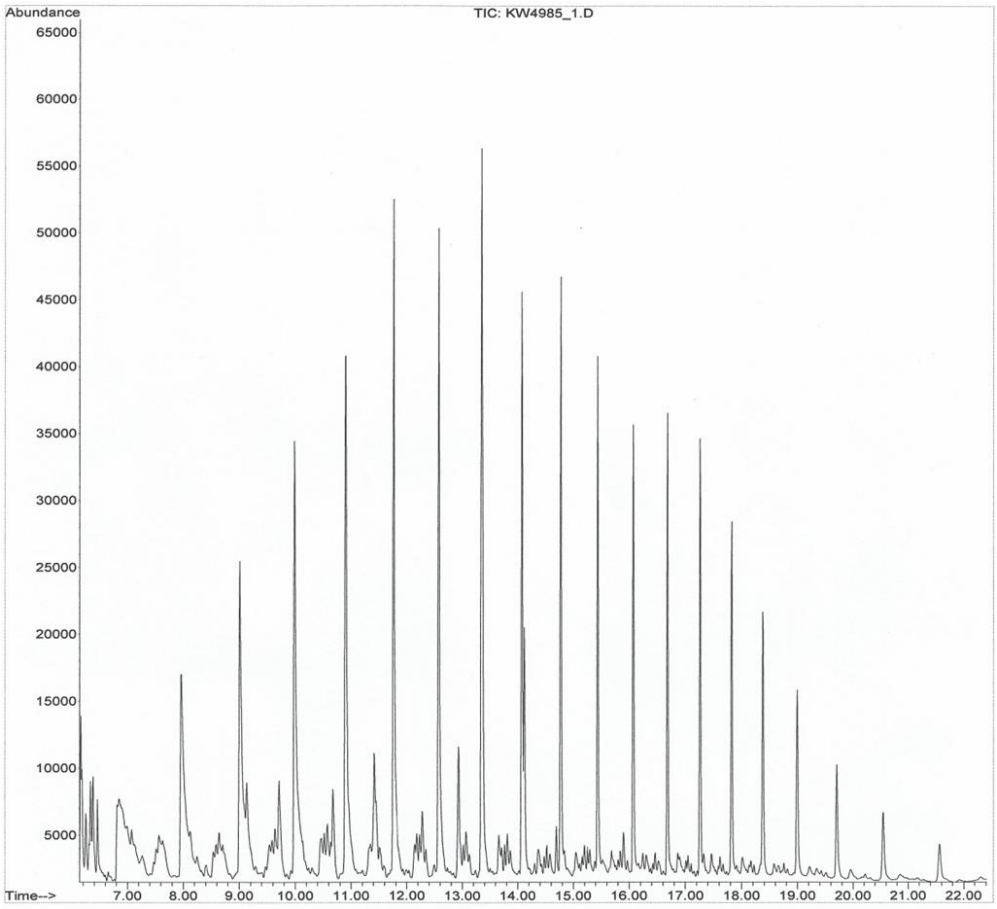


Figure 2-3: Chromatogram of TPH in crude oil

2.4 Conclusions

In this study a light crude oil of high API gravity and less viscosity is used. There is no significant difference of analyte concentration found between reference and non-preserved crude oil samples. This indicates that the material loss due to biodegradation during transport is negligible and hence makes no significant impact on the next steps of the study. The analyte concentrations found in this chapter will be used in calculations of oil-water partition coefficients in WAF, mass balances, etc. in the next sections.

3. Analysis of Water Accommodated Fraction of Oil

3.1 Introduction

Laboratory scale Water Accommodated Fraction (WAF) experiments under controlled conditions can give predictions about the fate of offshore oil spills (Faksness et al., 2008). This study examines oil-seawater partitioning patterns by carrying out WAF experiments at conditions which are analogous to the North Atlantic Ocean.

Crude oil obtained from a Newfoundland and Labrador offshore source (which was analyzed in the previous chapter) was used to prepare WAF under the guidelines by the modified CROSERF protocol (Barron and Ka'aihue, 2003; Singer et al., 1995) and WAF preparation instructions given by Singer et al. (2000).

As described in chapter one, there are a number of factors that can affect the oil-water partitioning behaviour. Further to those, mixing energy, light insensitivity and microbial activity among others are also involved in the fate of an oil spill. After reviewing the literature, the factors summarized in Table 3-1 were selected as key factors in this study. The partitioning behaviour of each oil component was studied by carrying out WAF runs at each of the levels outlined in Table 3-1.

Table 3-1: Factors and levels of the WAF experiments

Factor	Level	Reference
Time	24 h	(Barron and Ka'aihue, 2003; Singer et al., 2000a)
	72 h	
	168 h	
	240 h	
Temperature	4 ^{o}C	The typical temperature range of the North Atlantic Ocean (AMAP, 2010). (http://www.seatemperature.org/north-america/canada/torbay-january.htm)
	10 ^{o}C	
	15 ^{o}C	
Oil loading	0.1 g/L	(Barron and Ka'aihue, 2003; Singer et al., 2000)
	1 g/L	
	5 g/L	
	10 g/L	

3.2 Materials and methods

WAF experiments were carried out for ten days to allow the crude oil and seawater to reach equilibrium with each other. The equilibrium conditions were studied by carrying out experiments at different oil loadings and temperatures. Based on the results of that preliminary study the rest of the WAF experiments were planned and carried out by varying the factors and levels outlined in Table 3-1.

3.2.1 Glassware cleaning

The following glassware cleaning procedure (Modified ASTM 3325-90) was followed throughout the experiment.

1. All the brand new glassware was washed with concentrated HCl (H^+ ions) to neutralize any alkaline conditions and remove trace metals on the glass surface before using them for the first time.
2. Before each use, each of the glassware was rinsed with de-ionized water first.
3. They were soaked in a detergent water bath for a few hours and rinsed three times with plenty of de-ionized water.
4. Each of the glassware was washed with ethanol and then with dichloromethane, which was the solvent used in sample preparation.
5. They were allowed to dry overnight inverted on lab paper toweling.

3.2.2 WAF preparation

Crude oil and artificial (prepared) seawater of 35 ppt salinity were used to prepare WAF. It was easier to maintain sterilized conditions inside WAF bottles by using simulated seawater than using natural seawater.

The samples were prepared by following the below mentioned steps which were outlined based on the updated recommendations of CROSERF test methods (Barron and Ka'aihue, 2003; Singer et al., 2000).

- Simulated seawater of 35 ppt salinity was prepared in the laboratory by dissolving 52.5 g of sea salt (from Sigma-Aldrich) in 1.5 L of de-ionized water (Mukherjee et al., 2012).
- Pre-cleaned 2 L glass aspirator bottles were used with silicon/Teflon-lined stoppers. A tubing was attached to the bottom tap crane (above 3 cm from the base) that was used to remove WAF. A plastic clamp was used to stop outflow during the run.
- 1.5 L of simulated seawater was poured in to the aspiratory bottle allowing 25% head space.
- The incubator shaker (Innova 4230 Refrigerated Incubator Shaker by New Brunswick Scientific) was set to the required temperature. The bottle filled with seawater was fixed on the platform inside the incubator shaker with a metal clamp once after the incubator reached the required temperature. Figure 3-1 shows the arrangement.
- The required amount of crude oil (0.1 to 10 g of crude oil/ L of seawater) was poured smoothly on the water surface making turbulences as minimal as possible.
- The filled bottle was securely closed with a silicon/Teflon stopper.
- The sample was shaken at the speed of 120 rpm to provide the mixing energy so that it creates only a slight dispersion (Figure 3-1).
- The arrangement was allowed to mix in a dark environment continuously for ten days.

- A parallel controlled sample without any crude oil was run at the same conditions to compare the results.

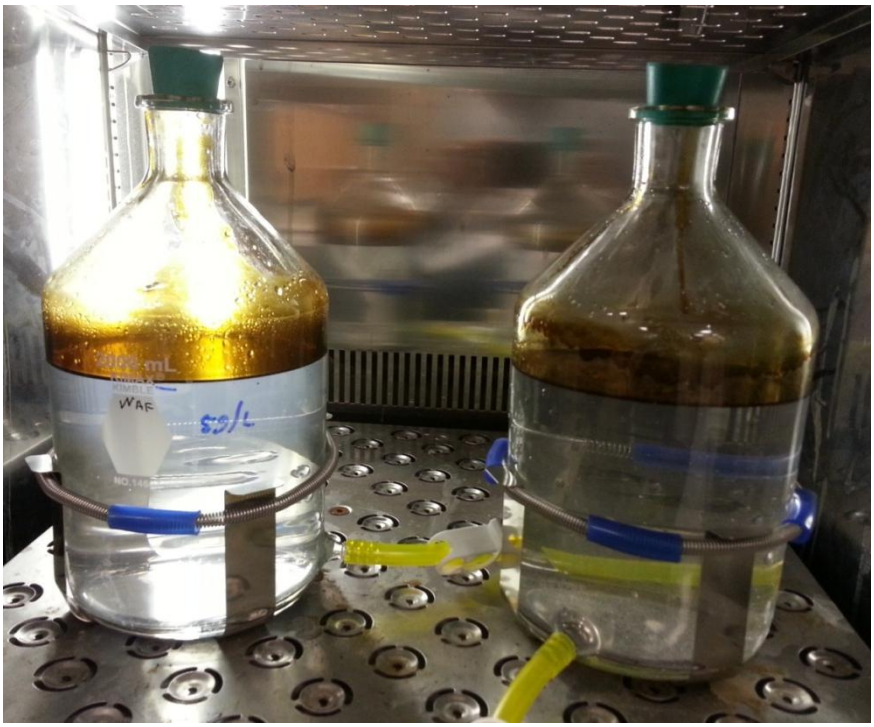


Figure 3-1: WAF bottle arrangement inside the incubator shaker

3.2.3 WAF sample collection

- A 100 mL WAF sample was taken out slowly from the bottom drainage valve after 0, 24, 72, 168 and 240 hours. 100 mL amber glass bottles were used for sample collection.
- The collected WAF samples were acidified to a pH of 2 with HCl to minimize the risk of biodegradation until analysis. The bottles were closed tightly with PTFE-

lined caps in such a way that the head space is as little as possible to minimize the interaction of the sample with air. The sample bottles were stored below 4 ^{o}C in a refrigerator (Kim et al., 2013) until chemical analysis was done.

3.2.4 Oil phase analysis after ten days

It was necessary to measure the concentrations of oil components in the oil phase for oil-water partition coefficient calculations. Therefore, the oil phase was separated immediately after collecting "day ten WAF".

The water was carefully drained out as much as possible from the bottom valve of the WAF bottle. The oil phase with some residual water was poured in to a separatory funnel. After allowing phase separation, the bottom water was removed through the bottom valve of the separatory funnel. A 100 mg of the remaining oil was weighed and dissolved in 100.00 mL of DCM to prepare a 1000 ppm oil sample. That sample was analyzed in the same way as described in section 2.2.4.

3.2.5 Chemical analysis of WAF

The chemical analysis of WAF was done according to the modified EPA 8270D method (Faksness et al., 2008; Kuhl et al., 2013; Neff et al., 2000). Samples were prepared for GC analysis as follows (modified EPA 3510).

- A 100 mL WAF was measured and put in to a pre-cleaned 250 mL glass separatory funnel.
- The sample was spiked with acenaphthene-d_{10} (IS).

- It was serially extracted three times with a total of 20 mL of DCM as shown in Figure 3-2.

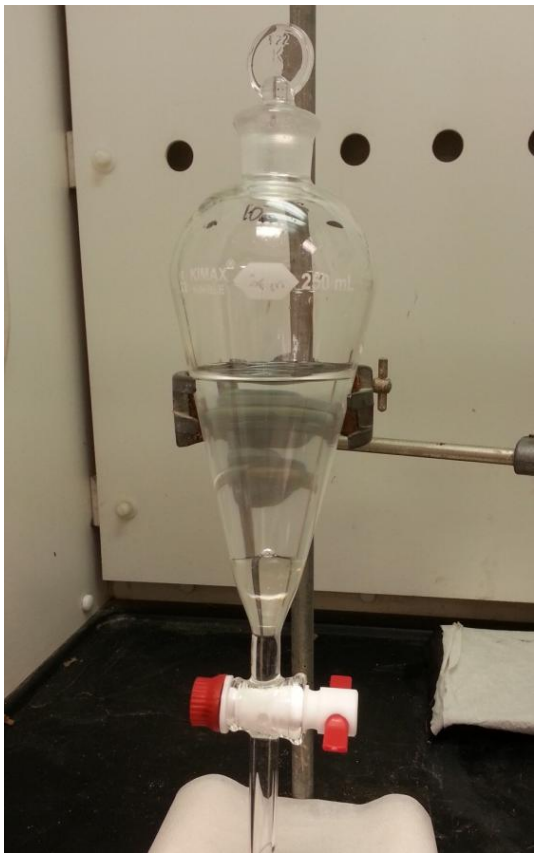


Figure 3-2: WAF extraction

- The anticipated concentrations of WAF were lower than that of crude oil. Therefore, the stock solution used in crude oil analysis was diluted to give more suitable standard addition curves for final measurements. Hence, the stock solution of PAHs described in Table 2-3 and the stock solution of phenols in Table 2-4 were diluted to 1% of their initial concentrations to be used in WAF standard additions.

- Similar to crude oil analysis, standard addition analysis was deployed to quantify the concentration of analytes. Four samples were prepared with different volumes of stock solution as explained in Appendix A.
- Separate samples were prepared for PAHs, phenol/alkylated phenols and TPH with corresponding stock solutions.
- The samples were analyzed by the GC-MS which was operated in the SIM mode. The methods used for each of the analyte group are there in Appendix.

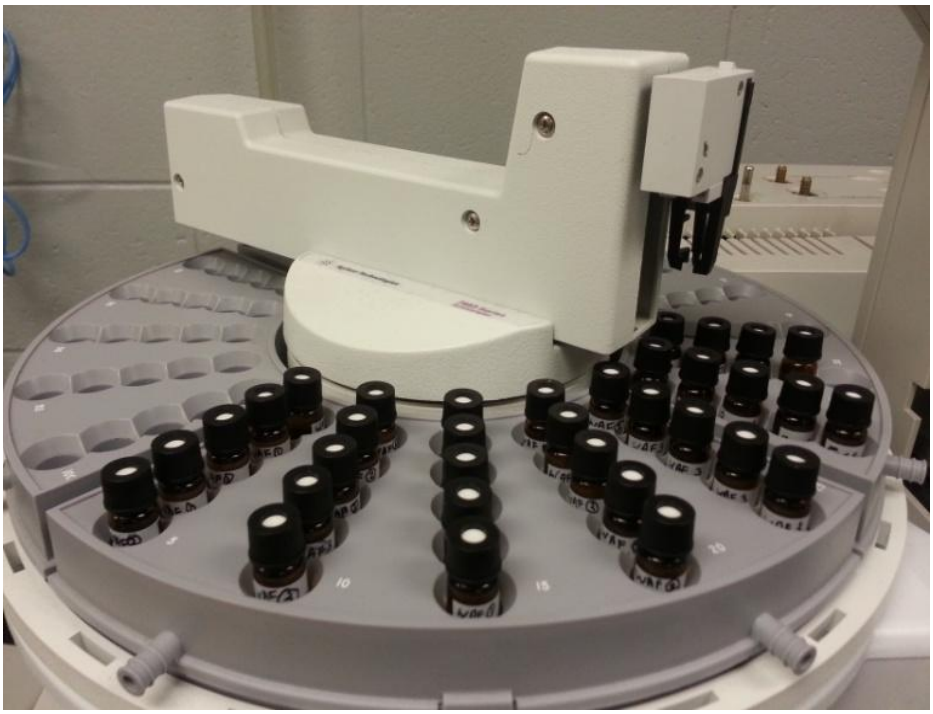


Figure 3-3: The samples on the auto sampler of the GC

A mass balance was done for the WAF system which was at 4 ^{o}C and oil loading of 10 g/L to determine if there were any mass losses. The total mass of each of the oil

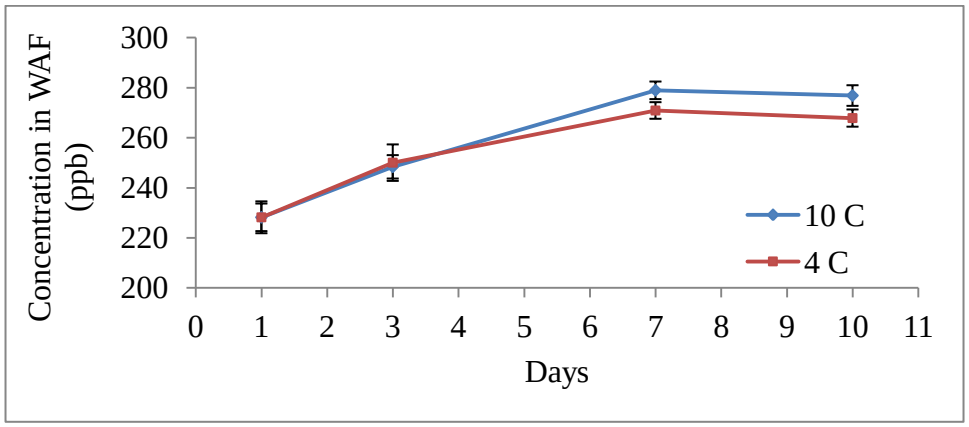
components in both the oil phase and water phase at day zero was considered as the mass input. The total mass in those two phases at day 10 was the mass output. The percentage loss was calculated by the difference of the input and output.

3.3 Results and discussion

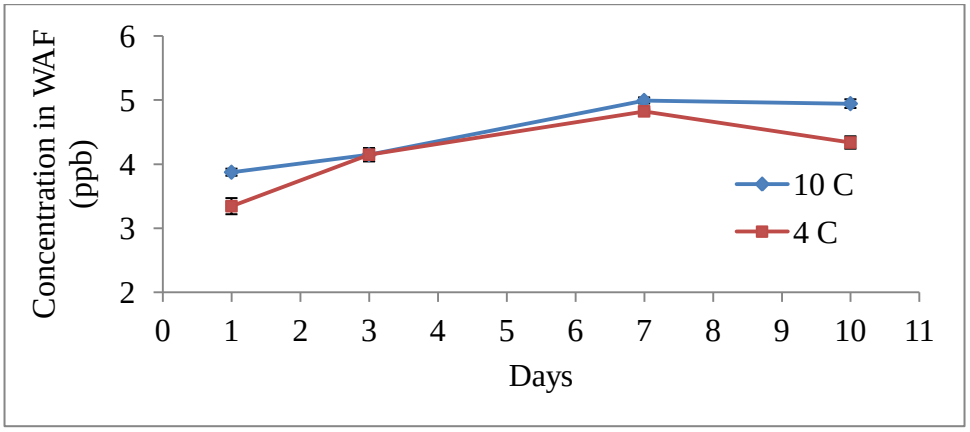
Oil-water partitioning bahaviour depends on both oil properties and environmental conditions. The oil-water partitioning is a weak function of salinity within small salinity changes possible in the ocean (Whitehouse, 1984), as such a fixed salinity was used in this study. The use of simulated seawater contributed in minimizing the biodegradation of the samples.

In preliminary stage of the experiment, different oil loadings (0.1 to 10 g/L) were studied to identify the minimum oil loading that can create a saturated WAF. WAF concentrations stabilized after 5 g/L oil loading. Therefore a 10 g/L was approximated as the oil loading that creates a saturated WAF at 10 ^{o}C and 120 rpm mixing speed. Given that outcome, all the below studies to find the effects of time and temperature were carried out with an oil loading of 10 g/L.

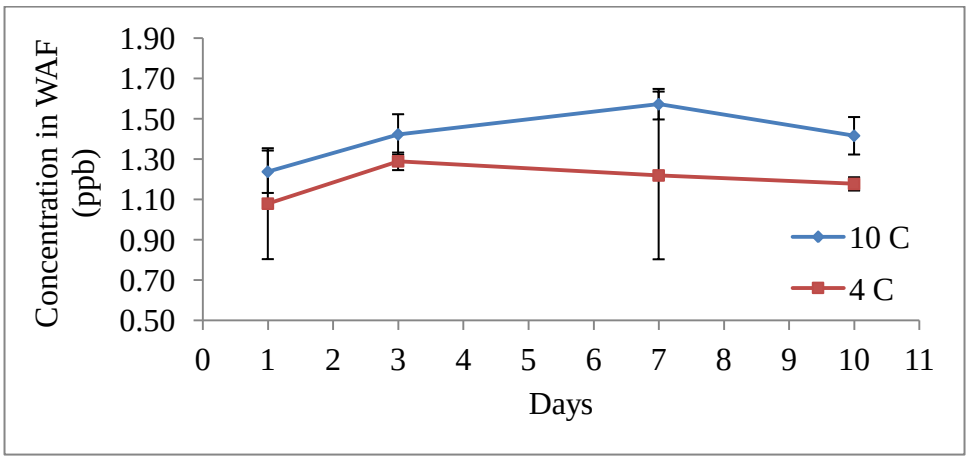
Figure 3-4 shows the change of the concentrations of each oil component with time at 4 ^{o}C and 10 ^{o}C. Naphthalene dominated in terms of the concentration in WAF at both the temperatures over the test period. The second highest concentration was phenol. A similar result was observed by Hokstad et al. (1999) who noted high concentrations of naphthalene and phenol and relatively small concentrations of larger PAHs in WAF.



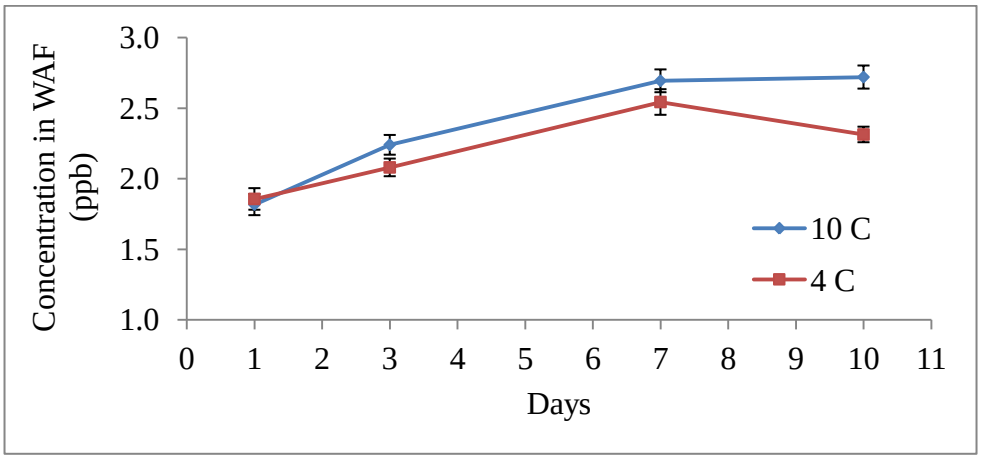
(a) Naphthalene



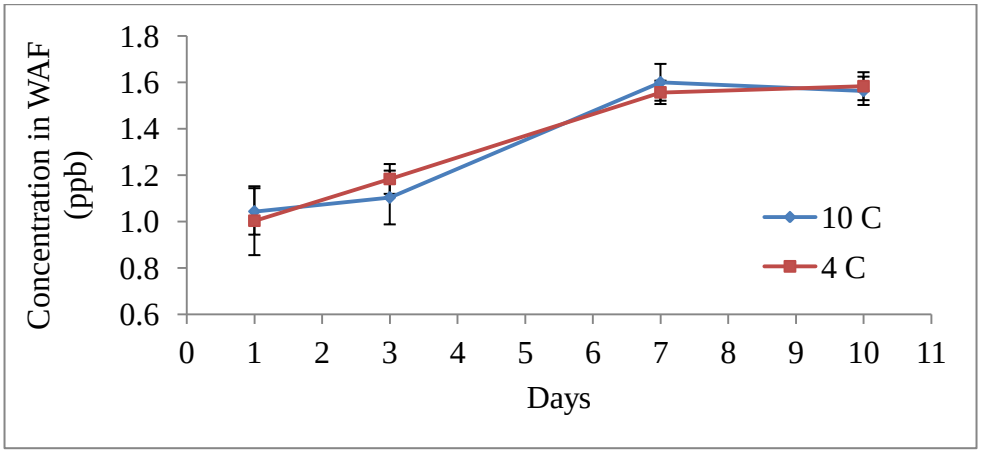
(b) Fluorene



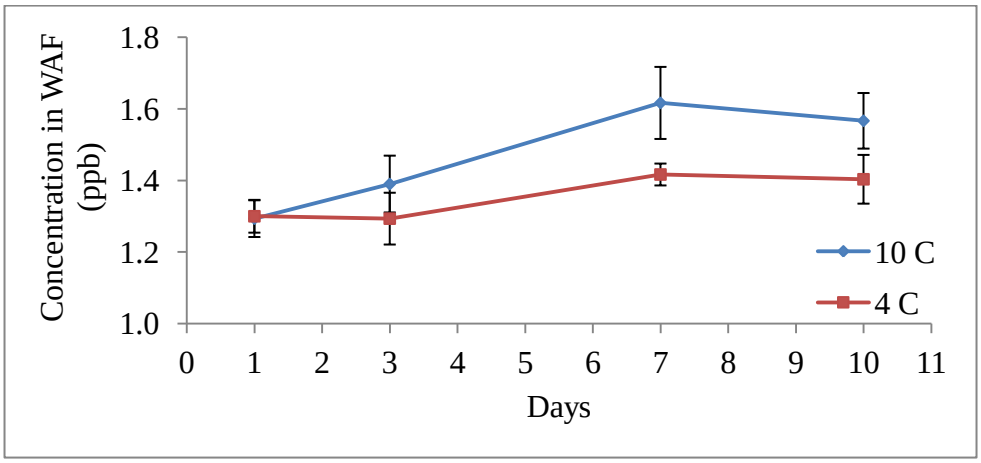
(c) Dibenzothiophene



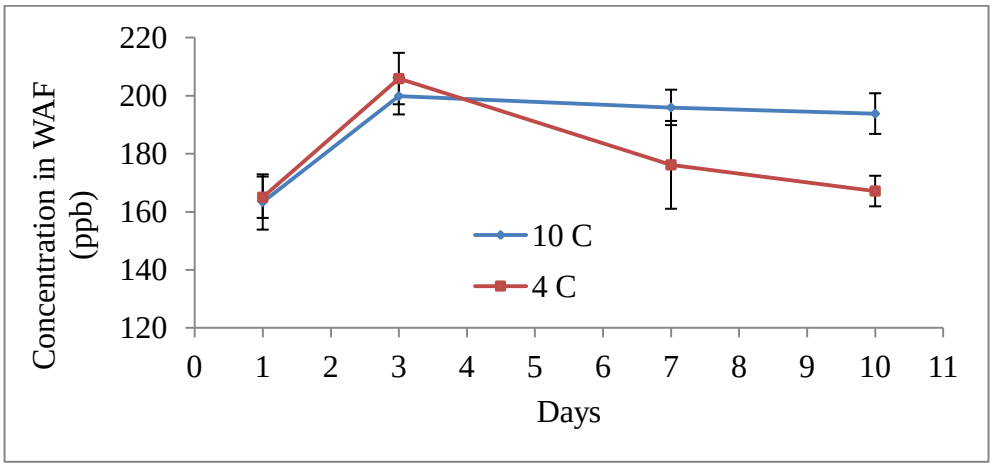
(d) Phenanthrene



(e) Pyrene



(f) Chrysene



(g) Phenol

Figure 3-4: Concentration of (a) naphthalene, (b) fluorene, (c) dibenzothiophene, (d) phenanthrene, (e) pyrene, (f) chrysene and (g) phenol in WAF as a function of time at 4 ^{o}C and 10 ^{o}C temperatures

Fluorene showed the third highest concentration in WAF while larger ringed PAHs were much lower (1-2 ppb). This is analogous to the finding by Sterling et al. (2003) who noted that larger molecular weight PAHs have lower solubilities in water. As the number of benzene rings increases the non-polarity and hydrophobicity of those PAHs also increases. That limits the ionization capability and as a result of that larger PAHs show lesser water solubility than smaller ones.

3.3.1 Effect of time

Naphthalene was the highest concentration in both crude oil and WAF relative to all the other target oil components. There was a gradual increase of its concentration in seawater during the first seven days and became constant after seven days at both the

temperatures. Similar behavior was observed in fluorene as well as in phenanthrene which are relatively larger PAHs with three benzene rings. The concentration of dibenzothiophene did not change much with time. Chrysene and pyrene (PAHs with four rings) behaved in a similar manner as naphthalene however the increase was less significant. Generally, all the above PAHs partitioned slightly more at 10 ^{o}C than at 4 ^{o}C. The concentrations became stable after seven days indicating an equilibrium state. Neff et al., (2000) found that PAHs take 60 hours (2.5 days) to reach equilibrium in an oil-water system. This can be even longer at lower temperatures (Faksness et al., 2008). Phenol showed an increasing partitioning up to the third day and then it became stable. Phenol reached its equilibrium state more quickly than other PAHs.

In Figure 3-5 and Figure 3-6 the concentrations of each of the analytes were normalized (concentration at the time of sampling/concentration at day one). Larger PAHs such as pyrene took longer to stabilize.

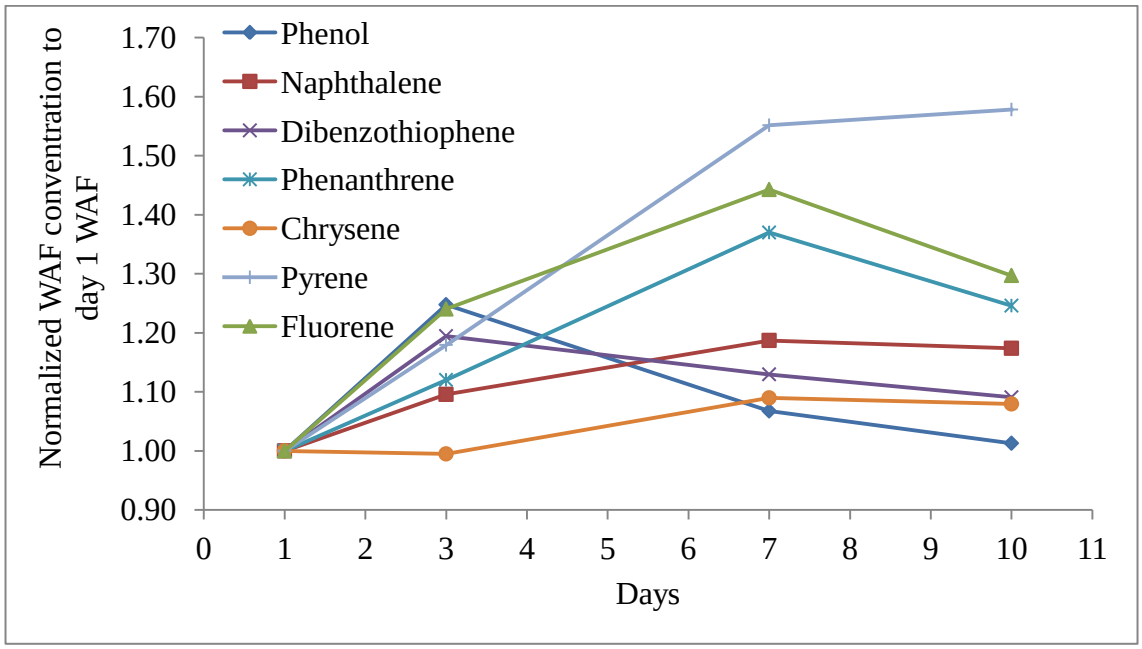


Figure 3-5: Normalized concentrations to the concentrations of day one WAF (at 4 ^{o}C and 10 g/L oil loading)

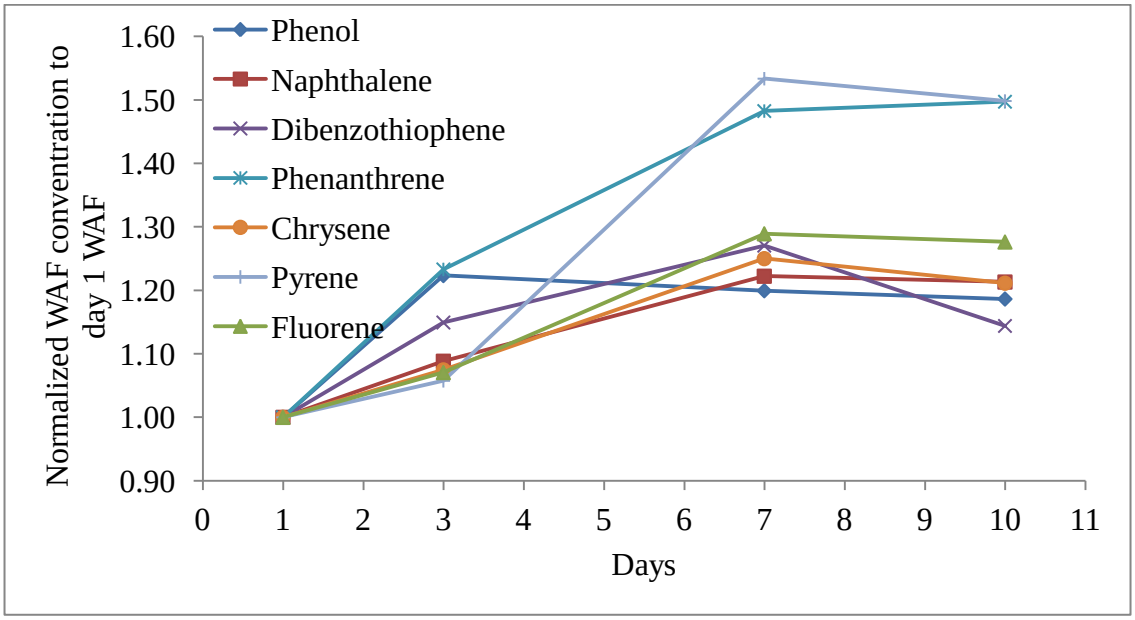


Figure 3-6: Normalized concentrations to the concentrations of day one WAF (at 10 ^{o}C and 10 g/L oil loading)

Table 3-2 presents the concentrations of analytes in fresh crude oil and weathered crude oil (oil at the ten day mark). The results showed that the concentration of oil components decreased with time. The possible reasons of this decrease will be discussed in the section of material balance.

Table 3-2: Analyte concentrations in fresh crude oil and day ten weathered crude oil

Analyte	Fresh oil (ppm)	Day 10 oil at 4 ^{o}C (ppm)	Day 10 oil at 10 ^{o}C (ppm)
Naphthalene	1109.95	845.74	853.97
Fluorene	278.82	238.64	233.75
Dibenzothiophene	25.69	20.56	20.17
Phenanthrene	454.23	398.14	402.73
Pyrene	32.85	27.42	27.75
Chrysene	57.19	52.85	51.56
Phenol	176.88	90.52	85.28

The concentrations in oil phase and seawater phase on day ten (assumed equilibrium concentrations) were used to calculate the partition coefficients (Log (K)) of each of the target oil components (Table 3-3). It also compares the experimental log (K) values with octanol-water partition coefficients (log K_{ow}) which are corrected for the temperatures and salinity.

Phenol, being a polar and relatively water soluble component had the lowest Log (K) value (2.73 at 4 ^{o}C and 2.64 at 10 ^{o}C). Naphthalene, the smallest PAH in this study, showed the second lowest log (K) (3.50 at 4 ^{o}C and 3.49 at 10 ^{o}C) indicating a higher availability in water phase than other PAHs. Taylor et al. (2010) also found that log (K) values were smaller than four for those small PAHs having one or two rings. Other larger PAHs had higher partition coefficients.

Table 3-3: A comparison of experimental and octanol-water partition coefficients

	At 4 ^{o}C		At 10 ^{o}C	
	Experimental	Octanol-water	Experimental	Octanol-water
Component	Log (K)	Log (K_{ow})	Log (K)	Log (K_{ow})
Naphthalene	3.50 ± 0.01	4.07	3.49 ± 0.01	3.90
Fluorene	4.74 ± 0.01	4.99	4.67 ± 0.01	4.81
Dibenzothiophene	4.24 ± 0.01	-	4.15 ± 0.03	-
Phenanthrene	5.24 ± 0.01	5.28	5.17 ± 0.01	5.13
Pyrene	4.24 ± 0.02	5.91	4.28 ± 0.02	5.75
Chrysene	4.58 ± 0.02	6.81	4.52 ± 0.02	6.56
Phenol	2.73 ± 0.01	1.58	2.64 ± 0.02	1.47

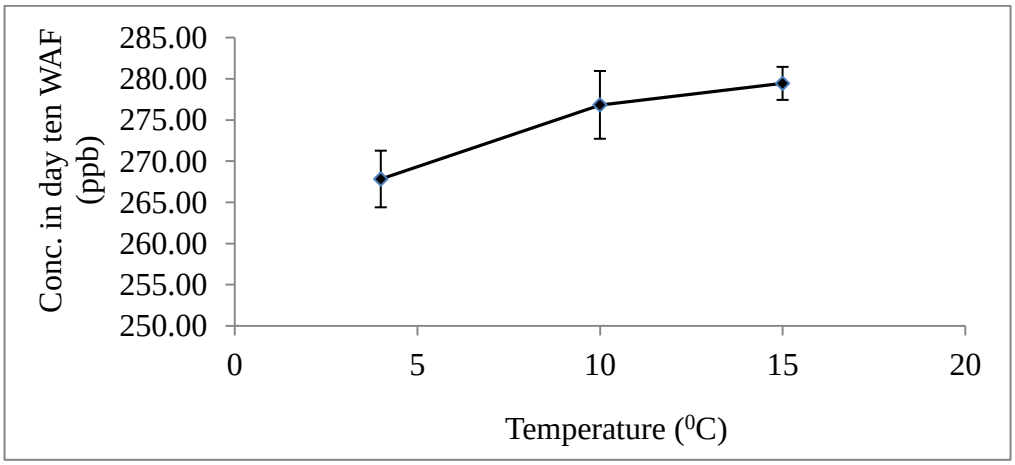
The log (K) value of naphthalene was much closer to the octanol-water partition coefficient at 10 ^{o}C than at 4 ^{o}C. Fluorene and phenanthrene also were in agreement at both temperatures. Pyrene and chrysene showed lower oil-water partition coefficients than the corresponding octanol-water partition coefficients indicating higher affinity for

water when they are were in an oil mixture versus in water as pure substances. Therefore, higher concentrations of the larger ringed PAHs can be expected in water than the concentrations obtained based on their octanol-water partition coefficients. The experimental coefficients obtained for phenol are a little higher than the octanol-water values indicating lower concentrations in the water phase than expected in theory. The complexity of crude oil would impact the partitioning and resulted the difference in those different two systems. The log (K_{ow}) considers an octanol-water system where the solute is its pure form. In this WAF arrangement, it was a crude oil and seawater system with hundreds of different solutes.

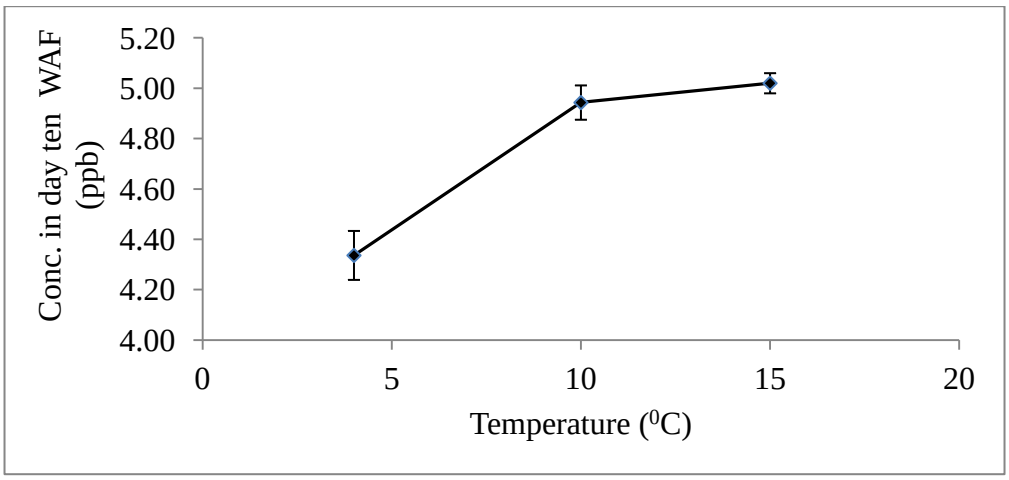
3.3.2 Effect of the temperature

Figure 3-7 summarizes the concentrations of seven target oil components as a function of temperature. The WAF prepared with 10 g of crude oil in 1 L of saline water (10 g/L oil loading) at day ten is shown.

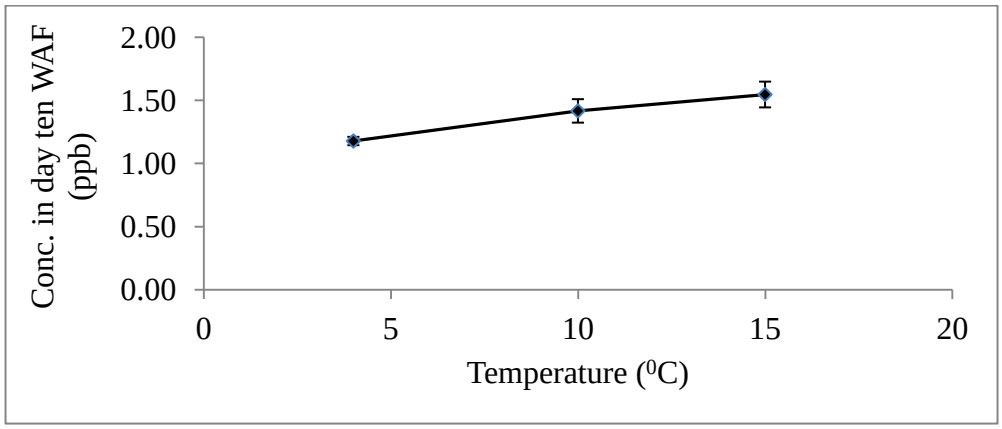
All PAHs, except pyrene, showed an increase of their concentrations in water as temperature increased from 4 ^{o}C to 10 ^{o}C. Pyrene was relatively constant if the experimental error was considered. Phenol increases up to 10 ^{o}C and then a slight decrease up to 15 ^{o}C.



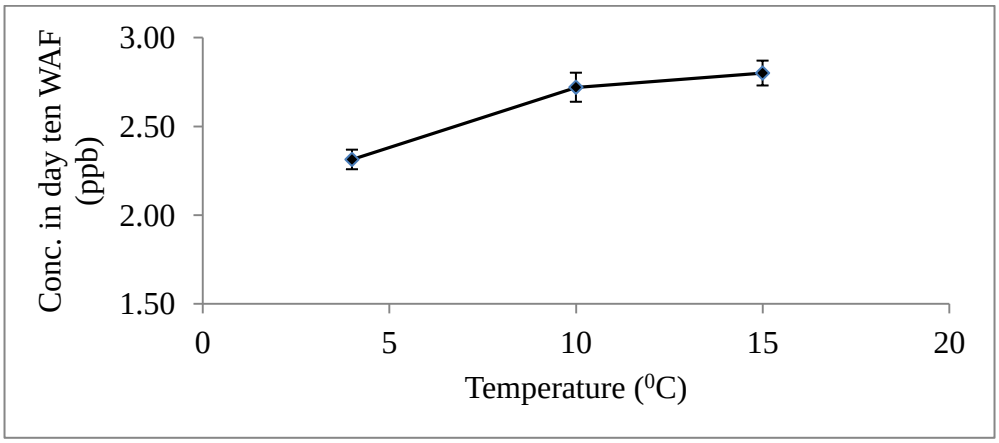
(a) Naphthalene



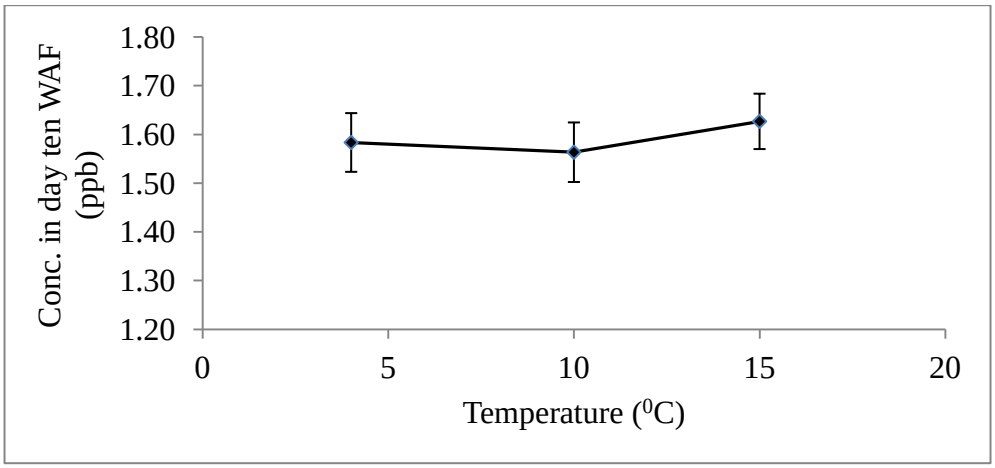
(b) Fluorene



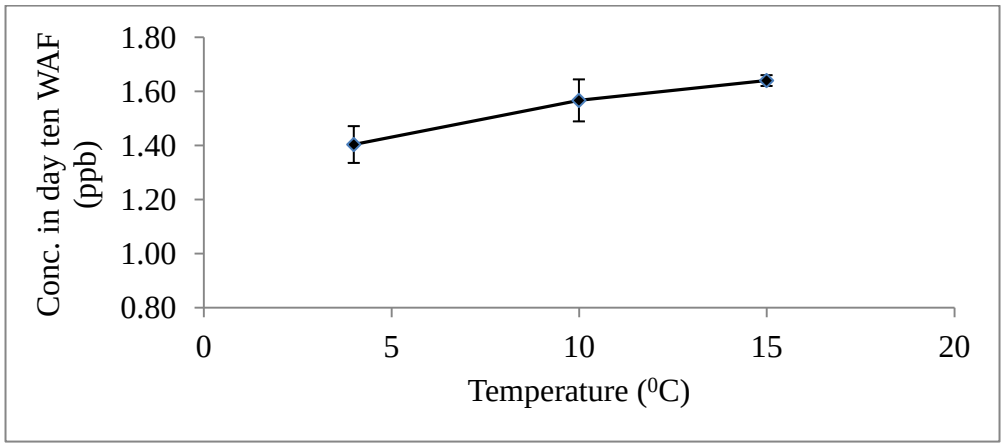
(c) Dibenzothiophene



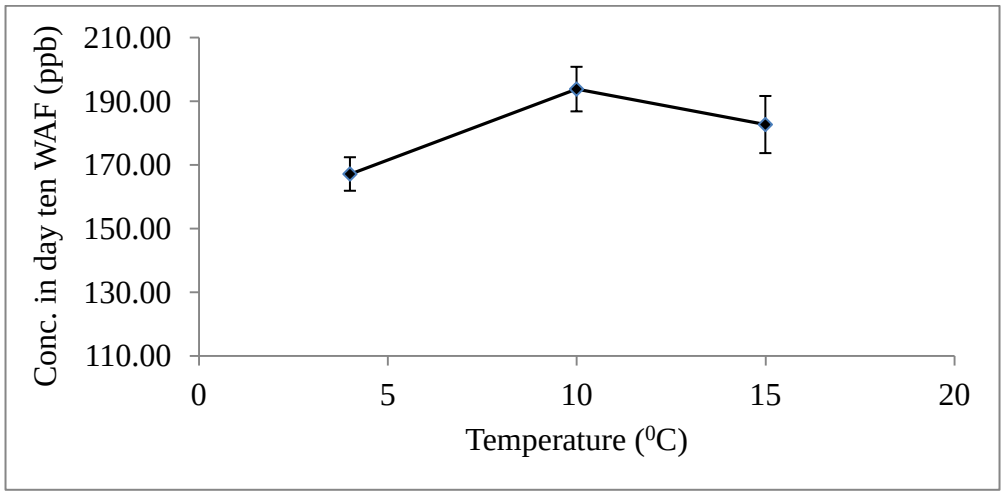
(d) Phenanthrene



(e) Pyrene



(f) Chrysene



(g) Phenol

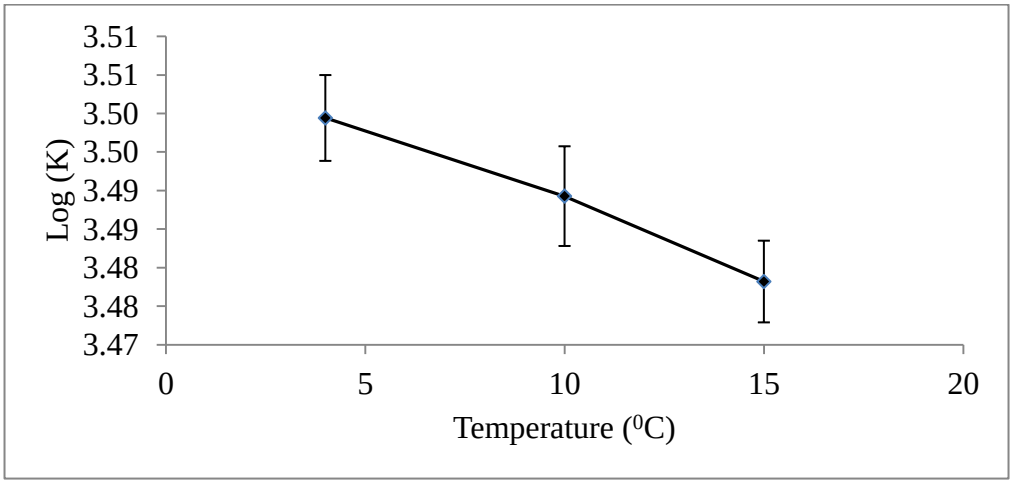
Figure 3-7: Day 10 WAF concentrations of (a) napthalene, (b) fluorene, (c) dibenzothiophene, (d) phenanthrene, (e) pyrene, (f) chrysene and (e) phenol as a function of temperature

Generally, an increased solubility of oil components was observed with temperature, which is not unexpected (Anderson et al., 1974; Faksness et al., 2008; Gearing and Gearing, 1982; Whitehouse, 1984), however, there have been few studies at these low temperatures.

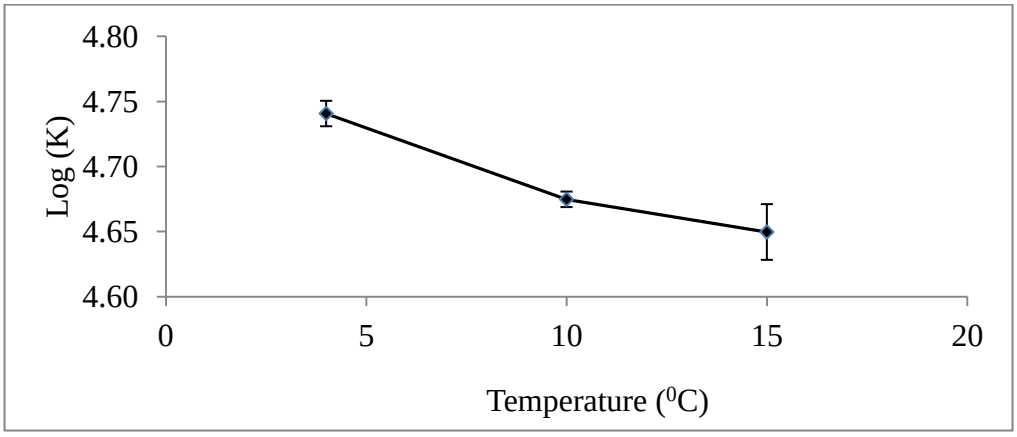
3.3.2.1 Oil-seawater partition coefficient with temperature

Oil-seawater partition coefficients were calculated at each of the three temperatures for each of the seven oil components. The day ten WAF results obtained above at 10 g/L oil loading were used for the calculation. Analyte concentrations in oil

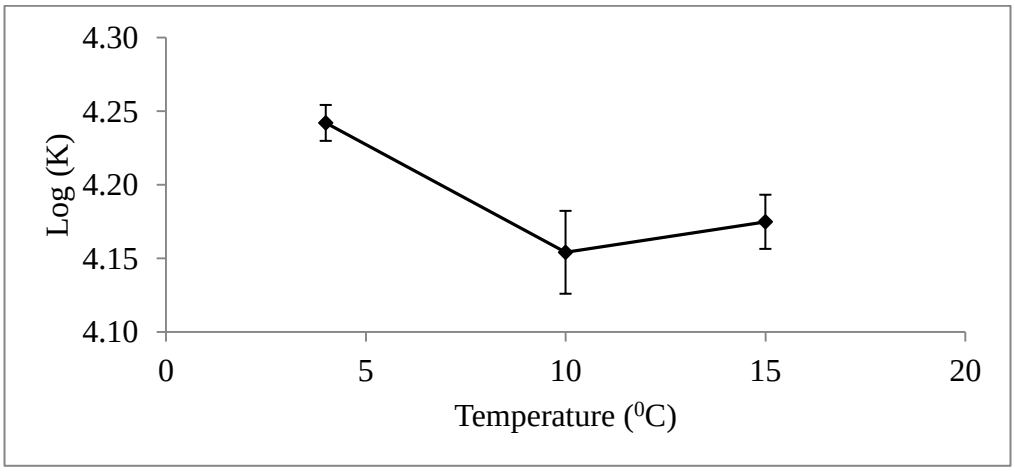
phase were found by analyzing the oil phase right after the day ten WAF is collected. Figure 3-8 shows the behaviour of partition coefficients as a function of temperature.



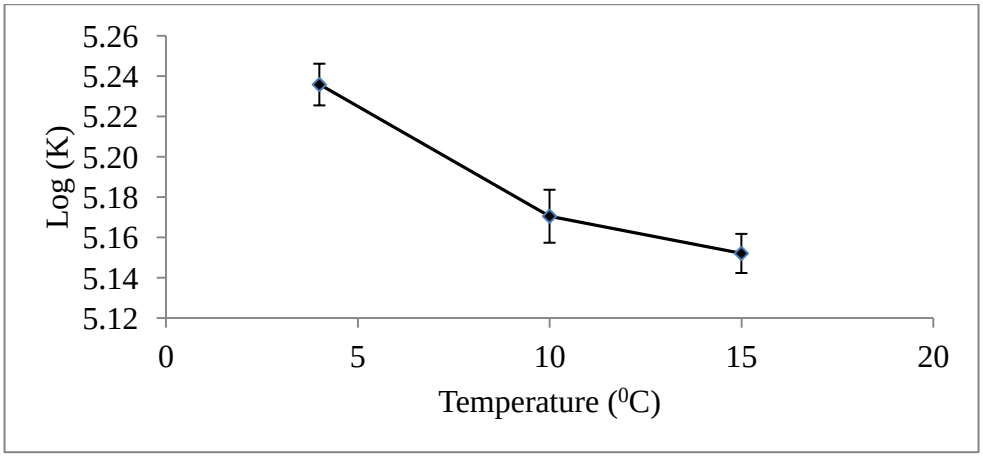
(a) Naphthalene



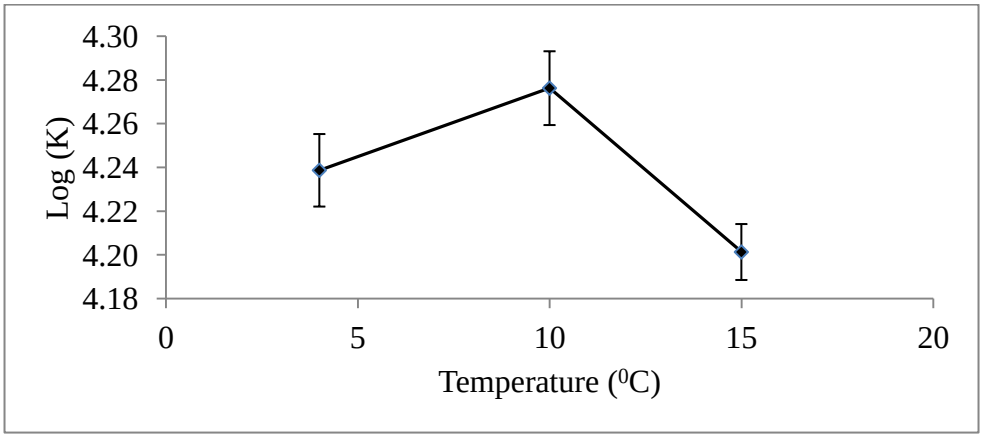
(b) Fluorene



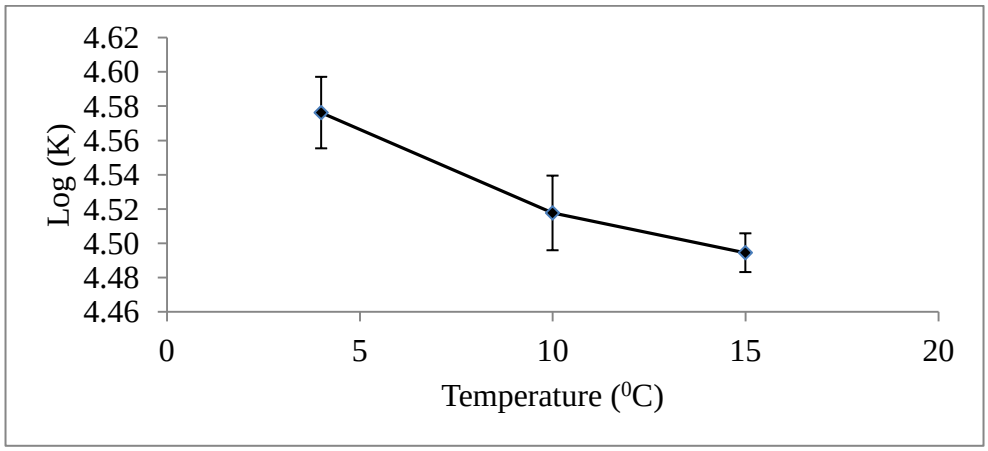
(c) Dibenzothiophene



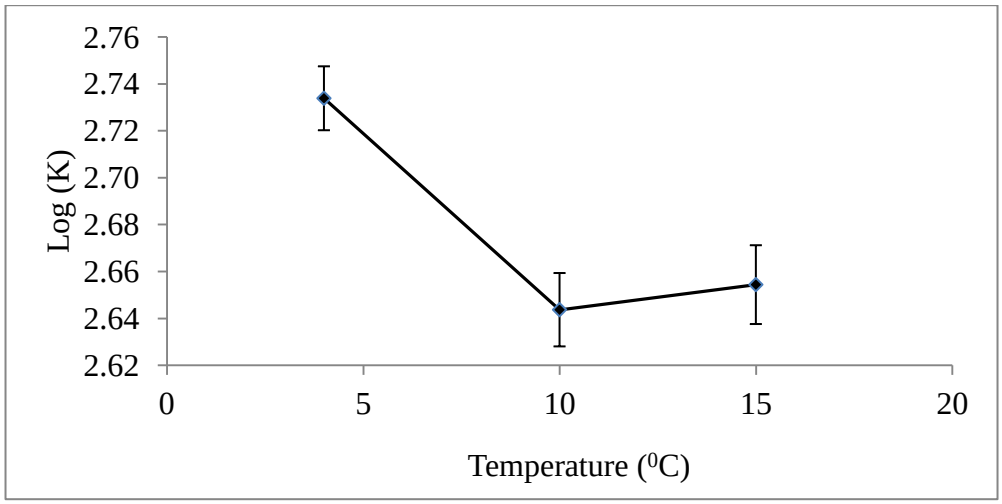
(d) Phenanthrene



(e) Pyrene



(f) Chrysene



(g) Phenol

Figure 3-8: Oil-seawater partition coefficients of (a) napthalene, (b) fluorene, (c) dibenzothiophene, (d) phenanthrene, (e) pyrene, (f) chrysene and (e) phenol as a function of temperature

The partition coefficients of naphthalene, fluorene and phenanthrene decreased as the temperature increased. The percentage decrease of naphthalene was 0.61% from 4 ^{o}C

to 15 ^{o}C and that was the smallest percentage decrease compared to the other PAHs and hence the least sensitive PAH to the temperature. The values reported for pyrene and dibenzothiophene deviate from that trend at 10 ^{o}C. However, the partition coefficient at 15 ^{o}C is clearly lower than that of at 4 ^{o}C for both. The percentage decrease of the concentrations of fluorene, dibenzothiophene, phenanthrene and chrysene were in the range of 1.58 ± 0.21% to 1.92 ± 0.18%. Pyrene indicated only a 0.88% decrease. The partition coefficient of phenol decreased as temperature increased from 4 ^{o}C to 10 ^{o}C and then increased slightly as the temperature further increased up to 15 ^{o}C. Overall, the partition coefficient decreased as the temperature increased from 4 ^{o}C to 15 ^{o}C if the experimental error is considered. The percentage decrease of phenol was 2.91% as temperature increased. This was the highest percentage compared to all the other analytes.

The same decreasing behavior was noticed in octanol-water partition coefficients presented in Table 1-8. Bennett and Larter, (1997) in their study observed a decrease in oil-seawater partition coefficients of alkylphenols as temperature increases from 25 ^{o}C to 80 ^{o}C.

Higher partition coefficients indicate low concentration of oil to seawater at cold temperatures. Therefore, a lesser availability of crude oil components such as PAHs and phenols is expected in seawater at lower temperatures compared to higher temperatures.

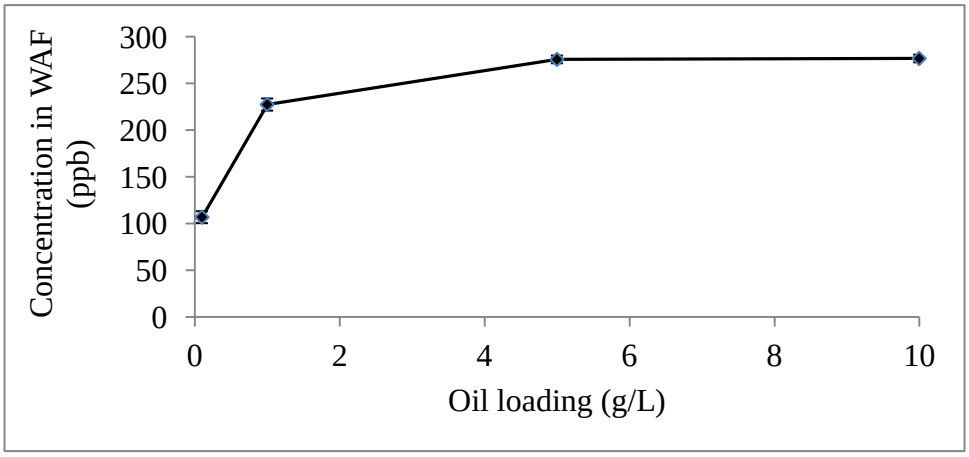
Because of their hydrophobic nature, PAHs show higher affinity for suspended particulate in the sea water. Therefore, they attach to those particulates and sediment on

the sea bed. As a result of that higher PAH concentration is expected in bottom sediment than in water (Moore and Ramamoorthy, 1984).

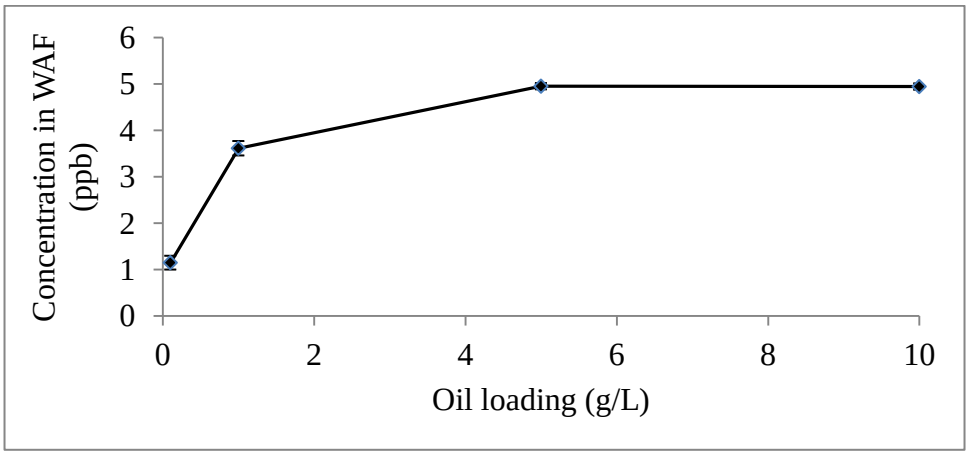
3.3.3 Effect of oil loading

Previous WAF studies used several oil loadings to identify a minimum oil loading that creates the maximum oil concentration in water (Barron and Ka'aihue, 2003). This is referred to as the minimum saturation oil loading. CROSERF procedures which are to standardize WAF experiments recommended a 1:40 oil:water ratio (25 g/L of seawater). It was later found to be much higher than the minimum saturation oil loading of 10 g/L at room temperature (Hokstad et al., 1999, 2000). Therefore, this study selected a oil loading range from 0.1 g/L to 10 g/L to study the effect of oil loading on oil partitioning in to seawater and the oil loading that creates a saturated WAF at cold temperatures.

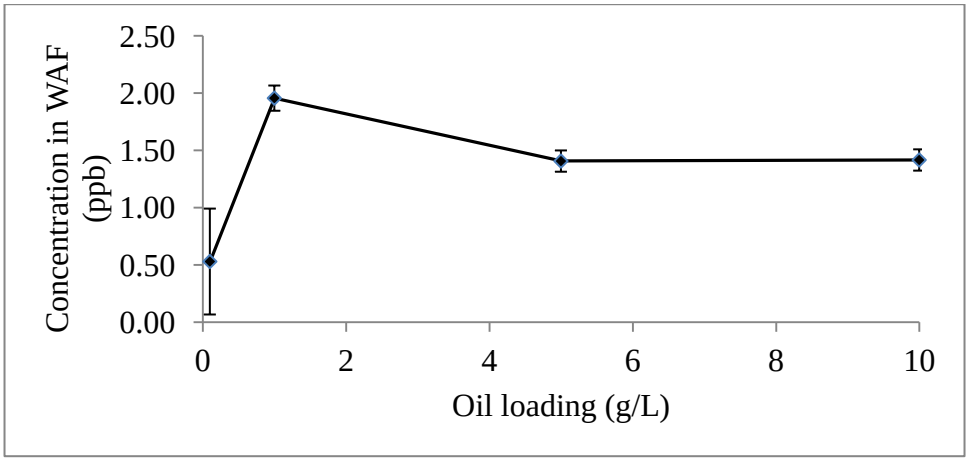
The data presented in Figure 3-9 outlines the concentration of each of the seven oil components as a function of oil loading. Analyte concentrations of day ten WAF at 10 ^{o}C were considered here.



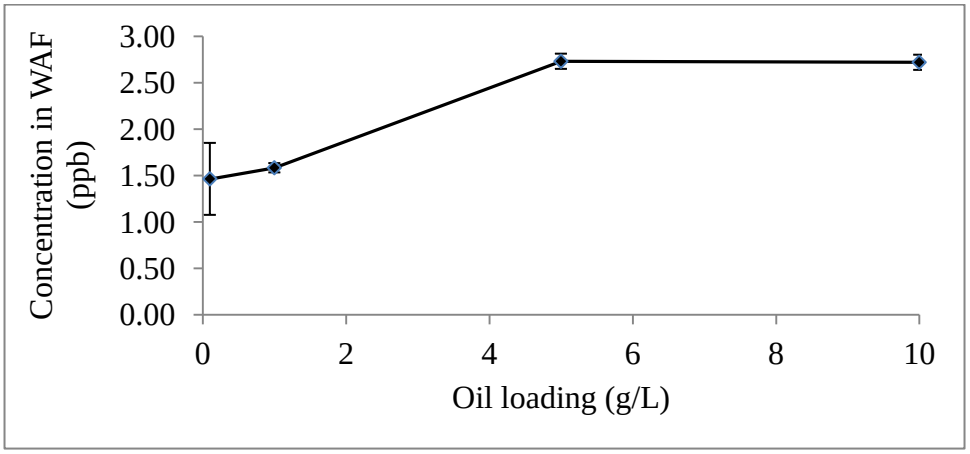
(a) Naphthalene



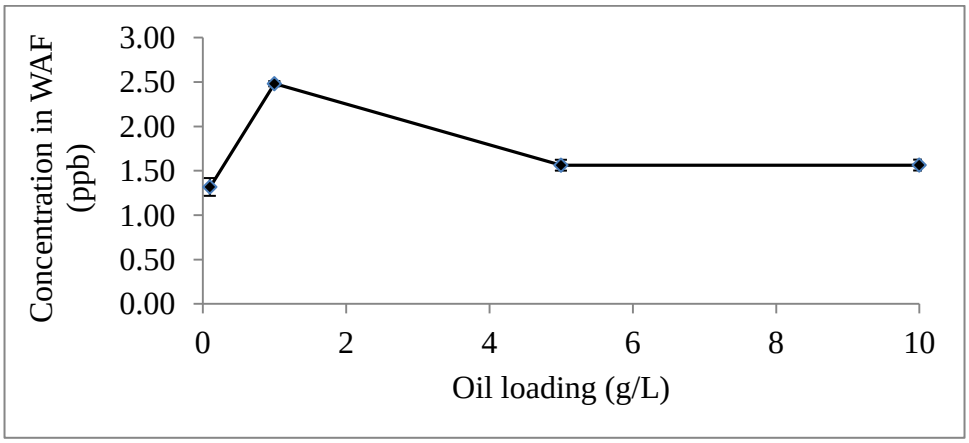
(b) Fluorene



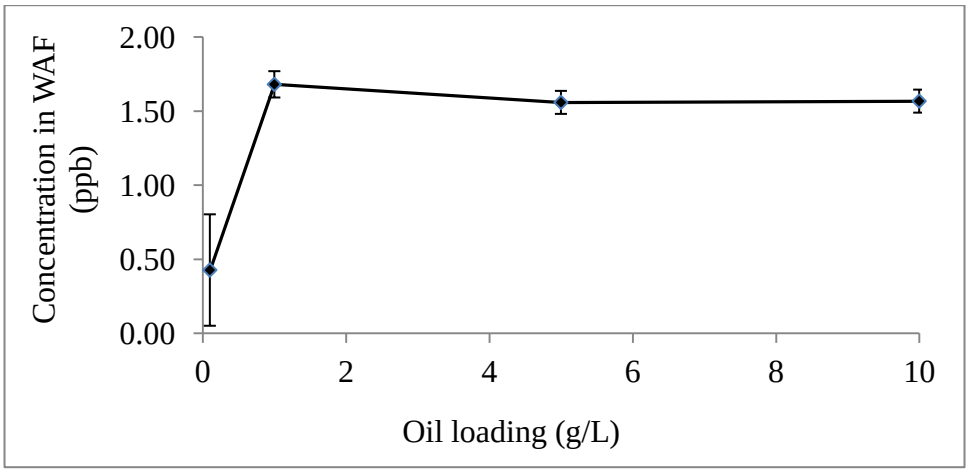
(c) Dibenzothiophene



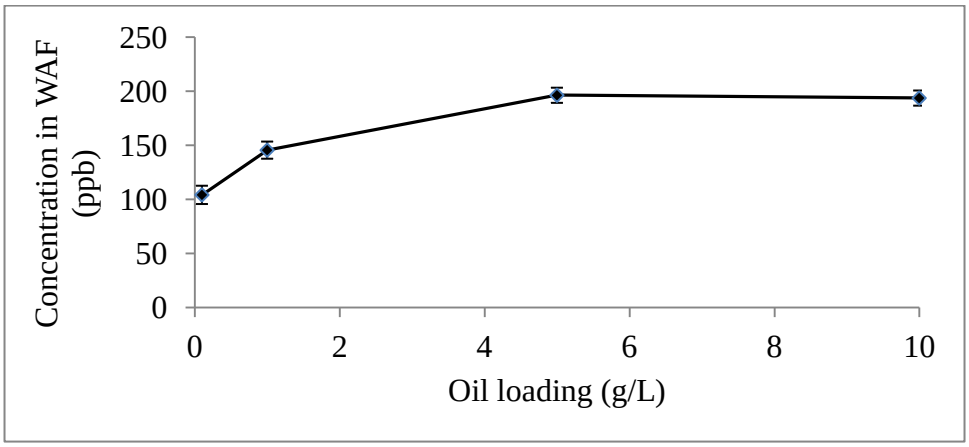
(d) Phenanthrene



(e) Pyrene



(f) Chrysene



(g) Phenol

Figure 3-9: WAF concentration of (a) napthalene, (b) fluorene, (c) dibenzothiophene, (d) phenanthrene, (e) pyrene, (f) chrysene and (e) phenol as a function of oil loading

According to the plots in Figure 3-9, concentrations of all the PAHs and phenol in seawater increased as oil loading increased from 0.1 g/L to 5 g/L. A increase of dibenzothiophene, pyrene and chrysene was observed at 1 g/L oil loading which decreased again at 5 g/L oil loading. This might be due to higher dispersion of oil into the water column at lower oil loadings. A thick oil layer was observed in WAF bottles at higher oil loadings such as 5 g/L and 10 g/L. The oil layer became very thin as well as dispersed in to water when the oil loading is low at the same mixing speed. Therefore higher oil dispersion can be expected when oil loading is small.

3.3.4 Mass balance

Table 3-4 summarizes the results of the mass balance done for the WAF system which was at 4 ^{o}C and the oil loading of 10 g/L.

Table 3-4: Mass balance for the WAF system at 4 ^{o}C and 10 g/L oil loading

Analyte	Mass in (mg)	Mass out (mg)	Loss%
Naphthalene	15.11 ± 0.18	11.27 ± 0.14	25.43
Fluorene	4.01 ± 0.05	3.07 ± 0.04	23.44
Dibenzothiophene	0.37 ± 0.04	0.27 ± 0.05	28.18
Phenanthrene	6.70 ± 0.25	5.12 ± 0.20	23.59
Chrysene	0.86 ± 0.09	0.68 ± 0.09	21.11
Pyrene	0.47 ± 0.02	0.35 ± 0.02	25.24
Phenol	2.63 ± 0.17	1.41 ± 0.11	46.26

Most of the PAHs reported a material loss of a 25% at day ten compared to day zero and 46.26% for phenol. The possible reasons for those losses and possible mechanisms of loss can be listed down as follows:

- Crude oil adhered to the inside walls of the glass bottles above and just below the water level. This oil amount was not totally accounted for when measuring final amounts of material by analyzing the remaining oil amount just after taking day ten WAF.
- Volatile components such as phenol and naphthalene could volatize.
- Some amount of hydrocarbons can be lost due to the biodegradation possible in WAF which have been run for extended time (Neff et al. 2000).
- Errors associated with GC-MS analysis, such as; changes happen to the column during the test period, method changes, impurities in the column etc.

The percentage errors associated with GC-MS were calculated by analyzing a standard sample of known concentrations. (The results are shown in Appendix.) The standard sample was prepared at an average concentration which is anticipated in WAF. The percentage error of phenol was 20.15%, which was the maximum compared to all the other analytes. The errors of the PAHs were in the range of 10 - 20%. Dibenzothiophene indicated an error of 18.78% which was the largest compared to other PAHs. Dibenzothiophene analysis indicated a large error percentage in previous crude oil analysis as well. This resulted in relatively large error bars in plots of dibenzothiophene.

The internal standard; acenaphthene-d_{10} showed the lowest error at 11.82% and was therefore used to adjust the concentrations of the target analytes by calculating response factors.

3.3.5 Analysis of alkylated phenols

Four of the selected alkylated phenols were analyzed in WAF at 10 ^{o}C and 10 g/L oil loading to estimate the partition coefficients as an extension to the above study of phenol. M-cresol and p-cresol were quantified together as a single analyte due to a technical difficulty encountered in separating them using the column and conditions applied.

Table 3-5 summarizes the concentrations of alkylated phenols in fresh crude oil at day zero and in weathered crude oil after a ten day WAF experiment at 10 ^{o}C. Similar to phenol, concentrations of alkylated phenols decreased as oil aged.

Table 3-5: Alkylated phenols in fresh and ten days weathered oil

Analyte	Fresh oil	Oil after ten days of WAF
	Concentration (ppm)	Concentration (ppm)
O-cresol	97.35 ± 4.98	54.18 ± 2.60
M/p-cresol	77.04 ± 4.68	34.73 ± 3.99
4-ethylphenol	90.85 ± 6.05	47.01 ± 5.65

The concentrations of alkylated phenols at day ten and the oil-water partition coefficients calculated based on day ten concentrations are presented in Table 3-6.

Table 3-6: Oil-water partition coefficient of alkylated phenols

Analyte	Day ten WAF	
	Concentration (ppb)	Log (K)
O-cresol	62.38 ± 4.06	2.94 ± 0.05
M/p-cresols	32.52 ± 4.02	3.03 ± 0.10
4-ethylphenol	41.75 ± 5.55	3.05 ± 0.08

The highest concentration recorded for alkylated phenols in WAF is o-cresol. 4-Ethylphenol was present in 41.75 ± 5.55 ppb concentration, while both m- and p-cresols recorded the minimum concentration in the water phase. The partition coefficient of o-cresol was 2.94 ± 0.05 which is closer to the value obtained for phenol at the same

conditions (2.64 ± 0.01). Both m/p-cresols and 4-ethylphenol recorded comparatively higher partition coefficients than phenol and o-cresol.

The same experimental errors and material losses discussed earlier are applicable for alkylated phenols as well.

3.3.6 TPH analysis

Total petroleum hydrocarbon of WAF were measured to determine how closely associated TPH is with the various analytes tested. TPH was measured in WAF at 10 ^{o}C at two different oil loadings of 1 g/L and 10 g/L.

Figure 3-10 presents the TPH concentration in WAF as a function of time at two different oil loadings.

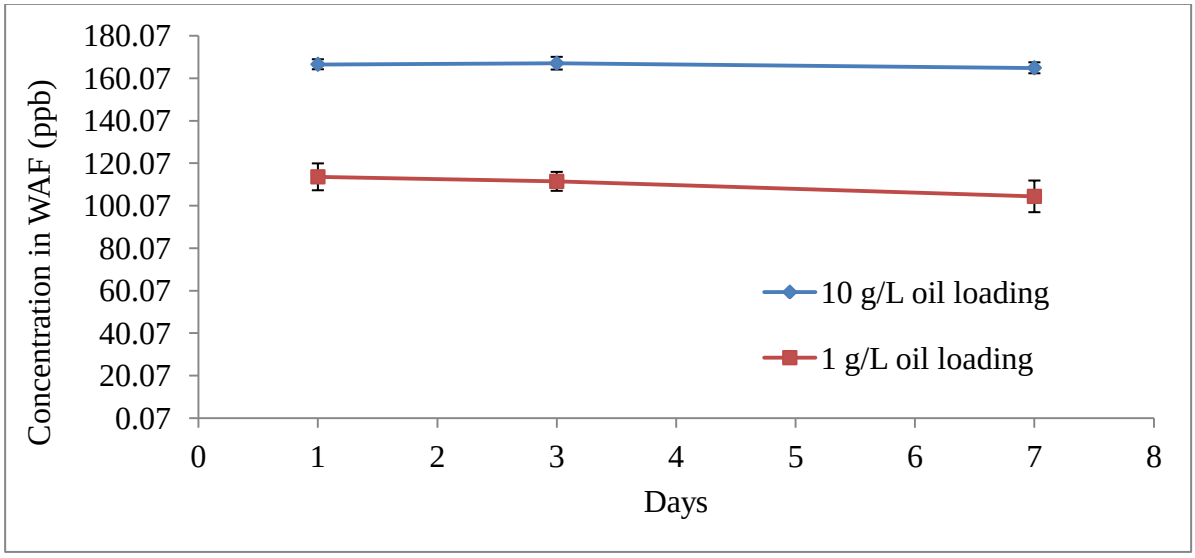


Figure 3-10: TPH concentration in WAF as a function of time at two different oil loadings at 10 ^{o}C

As the oil loading increased from 1 g/L to 10 g/L the TPH concentration increased significantly in WAF throughout the test period which agrees with the results from Sterling et al. (2003). In the Sterling study, TPH increased from 1 ppm to 100 ppm in WAF as the oil loading increased from 1 mL to 10 mL in 20 mL (approximately 43 g/L to 430 g/L) of simulated seawater at 30 ppt salinity.

At 10 g/L oil loading the TPH concentration was found to be almost stable with time.

In Figure 3-11 the normalized concentrations (concentration at the time of sampling/concentration at day one) of PAHs and phenol were compared with normalized TPH.

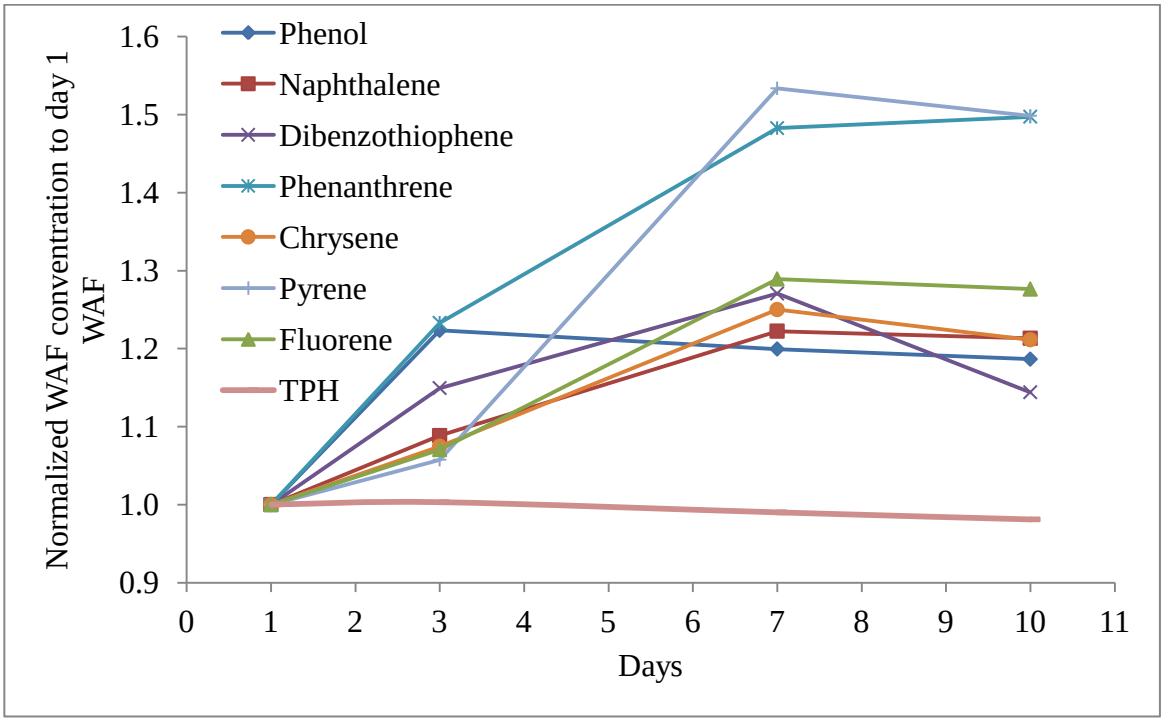


Figure 3-11: Normalized WAF and TPH concentrations at 10 g/L oil loading and 10 ^{o}C

The TPH was constant over the test period while the concentrations of the PAHs and phenol increased. Therefore, even though the TPH concentration remained constant the availability of PAHs and phenol in water column could be increased with time.

3.4 Conclusions

This WAF study was performed at colder temperatures, focusing on harsh the North Atlantic Ocean conditions. Partitioning of six of the key PAHs, phenol, alkylated phenols and TPH were studied in WAF which was prepared by mixing crude oil in artificial seawater of 35 ppt salinity. Naphthalene was the dominant PAH found in both the crude oil and WAF. Smaller PAHs such as fluorene and phenanthrene were there in the water phase in relatively higher concentrations than larger PAHs such as pyrene and chrysene. Phenol, being a relatively polar organic compound, was also detected in relatively higher concentration in both crude and WAF.

From the preliminary studies, it was found that WAF concentrations of most of the target oil components increase with time up to seven days and then reach an equilibrium state. Phenol reached the equilibrium even sooner than PAHs. Phenols and smaller PAHs such as naphthalene readily partitioned into the seawater being available significantly than other larger PAHs. However, the concentrations of phenol and naphthalene decreased drastically in the oil slick of WAF which in return affected their concentrations in water.

The smallest oil-water partition coefficient (Log K) 2.64 ± 0.02 was recorded by phenol while naphthalene recorded the secondly smallest coefficient 3.49 ± 0.01 at 10 ^{o}C

and 10 g/L oil loading. Phenanthrene recorded a oil-water partition coefficient of 5.17 ± 0.01 at 10 ^{o}C which was rather higher than corresponding Log K_{ow} value. Partition coefficients of larger PAHs such as pyrene (average Log K = 4.2) and chrysene (average Log K = 4.5) were found to be little smaller than corresponding Log K_{ow} values. Experimental errors and material losses might be a factor in some of those outliers.

The oil loading of 10 g/L made a saturated WAF system at the considered temperature range. Therefore the oil-water partition coefficients were calculated with WAF of an oil loading of 10g/L assuming saturated conditions.

Increase of the temperature from 4 ^{o}C to 15 ^{o}C increased the solubility of oil components in seawater which decreased the partition coefficients in return. This temperature increment decreased partition coefficients of phenol and naphthalene by 2.9% and 0.6% respectively. Phenol was the oil component that indicated the highest sensitivity to temperature. Log (K) of naphthalene decreased by 0.61% as temperature increased from 4 ^{o}C to 15 ^{o}C which was the smallest percentage change among other PAHs.

TPH concentration (alkanes from C8 to C34 with UCM) was found to be almost constant throughout the test period and did not correlate well to the other analytes. While the TPH remained constant PAHs and phenols increased in water column with time. TPH was found to be higher for the higher oil loading of 10 g/L than 1 g/L.

As a conclusion, it can be summarized that smaller PAHs and phenols are abundant in seawater during the first week after an oil spill. Larger PAHs take some time to partition into the water column and they are in lesser concentrations than those of

smaller ones. However, they are more persistent in both the oil phase and the water phase. The oil partitioning increases a slightly as temperature increases from 4 ^{o}C to 15 ^{o}C. The amount of oil spilled in offshore is an important factor that decides the oil availability in the seawater column. Heavy oil loadings may create a thick oil slick on top of the water enhancing the risk of surface and onshore contaminations.

4. Chemically Enhanced Water Accommodated Fraction of Oil

4.1 Introduction

Chemical dispersant application is the preferred oil spill mitigation response in energetic oceans (Fiocco and Lewis, 1999). Chemical dispersants are surface active agents (surfactants) that have both hydrophilic and hydrophobic properties (Mukherjee et al., 2012). They are capable of making small oil water micelles and of enhancing the dispersion process of oil into the water column (Brandvik and Daling, 1998) to prevent thick oil slicks on the surface of the water (Kuhl et al., 2013). Chemical dispersants change the partitioning behaviour of oil into seawater and affect the fate of oil spills.

In the previous study of the Water Accommodated Fraction (WAF) of oil the oil partitioning was studied under mechanical mixing. In this chapter the impact of chemical dispersants on the oil partitioning is studied, this is also called the Chemically Enhanced Water Accommodated Fraction (CEWAF) of oil. In CEWAF, the oil partitioning is enhanced by both mechanical mixing and chemical dispersants. A comparison of WAF and CEWAF is done to determine the change of the bioavailability of oil components in seawater due to the application of chemical dispersants in an oil spill. As an extension to the WAF study, the effect of time, temperature and oil loading on oil partitioning are studied in CEWAF.

4.2 Materials and methods

All the glassware was cleaned by following the procedures described in section 3.2. The CEWAF preparation was done according to the updated CROSERF protocol (Aurand and Coelho 2005; Singer et al., 2000). The simulated seawater was prepared at the salinity of 35 ppt by dissolving sea salt (by Sigma-Aldrich) in deionized water. The same incubator shaker used in WAF studies, Innova 4230 Refrigerated Incubator Shaker by New Brunswick Scientific, was used to control temperature and provide the samples with the mixing energy. The temperature of the incubator shaker was set to the required level and allowed to reach the temperature before starting each run.

1.5 L of seawater was added to a pre-cleaned aspiratory bottle which was fixed on the platform of the incubator shaker (similar to WAF preparation). The required amount of crude oil was added on top of the seawater creating as minimal as vortex.

The CEWAF was prepared using the chemical dispersant COREXIT EC9500A from Nalco Environmental Solutions TX, USA. The dispersant was added (dispersants:oil ratio of 1:10 (v/v)) on the floating oil using a Fisher Brand Elite 100 - 1000 μL micro pipette. The CEWAF bottle was secularly closed with a PTFE-lined stopper. The CEWAF sample was shaken at a speed of 120 rpm at the required temperature for ten days.

A 100 mL CEWAF sample was collected slowly from the bottom valve of the bottle at 0, 24, 72, 168 and 240 hours. Before each sample collection, the CEWAF was allowed to settle for one hour. The factors and levels considered in the CEWAF experiment are presented in Table 4-1.

Table 4-1: Factors and levels of the CEWAF experiment

Factor	Level
Time	24 h
	72 h
	168 h
	240 h
Temperature	4 ^{o}C
	10 ^{o}C
	15 ^{o}C
Oil loading	1 g/L (Dispersant 0.175 mL*)
	10 g/L (Dispersant 1.75 mL*)

(*The density of crude oil = 0.8553 g/mL)

The collected CEWAF samples were acidified to a pH of 2 with HCl to minimize the biodegradation before analysis. The bottles were closed tightly with PTFE-lined caps in such a way that the head space was at a minimum to minimize the interactions of the sample with air. The sample bottles were stored below 4 ^{o}C in the refrigerator (Kim et al., 2013) until analyzed.

The CEWAF was extracted three times with a total of 20 mL of dichloromethane (DCM) (Figure 4-1). The anticipated concentrations of CEWAF were lower than that of crude oil but higher than WAF. Hence, the stock solution of PAHs described in Table

2-3 and the stock solution of phenols in Table 2-4 were diluted to 10% of their initial concentrations to be used in CEWAF standard additions.

Figure 4-1: Extraction of CEWAF (left: CEWAF of 10 g/L oil loading, right: CEWAF of 1 g/L oil loading) with 20 mL of DCM

The chemical analysis of CEWAF was done in the same way as WAF analyses were done. The standard additions were done by preparing four samples as shown in the Appendix. The compositions of the four samples were decided in such a way that their final concentrations are in the detectable range with the GC methods developed for

previous WAF analysis. The samples were analyzed by the GC-MS in the SIM mode. The GC methods were the same as those used for WAF analysis and are presented in the Appendix.

Enhanced dispersion weakened the phase separation and as a result of that no explicit oil and water phases were seen after the settling time. Therefore the concentrations of the analytes were studied rather than calculating the partition coefficients.

4.3 Results and discussion

Figure 4-2 shows the behaviour of crude oil and seawater with the application of the chemical dispersants in the WAF bottles. The oil floated on top of the seawater as a thin slick as soon as oil was added to the water surface (picture A). Picture B was taken just after adding chemical dispersants on top of the oil slick. The slick was broken and the oil gathered along the wall of the WAF bottle as a ring. Picture C shows the plume of the oil which was formed on top of the water after ten minutes of mixing. The plume was created by the oil-water droplets which started dispersing into the water with the help of mixing energy. A complete crude oil-water dispersion was observed after 24 hours' mixing, as shown in picture D. The CEWAF samples were taken out for chemical analysis after one hour's settling time. Crude oil did not separate in as clear a phase as it did in WAF but a dense top plume was created which looked similar to the plume shown in picture C of Figure 4-2.

Figure 4-2: The crude oil-seawater behaviour with chemical dispersants

4.3.1 The effect of chemical dispersants on oil partitioning

Table 4-2 summarizes the ratios of analyte concentrations between CEWAF and WAF at the same conditions, showing relative changes of the concentration of each analyte due to the application of the chemical dispersant.

Table 4-2: Ratios of concentrations of CEWAF to WAF at 10 g/L oil loading at 10 ^{o}C

Analyte	CEWAF:WAF			
	Day 1	Day 3	Day 7	Day 10
Naphthalene	9.20	8.66	7.97	7.90
Fluorene	8.27	8.18	6.70	6.84
Dibenzothiophene	20.18	18.67	18.31	21.00
Phenanthrene	19.64	15.84	13.71	12.55
Chrysene	23.43	21.79	19.59	19.68
Pyrene	29.52	28.98	22.78	20.72
Phenol	5.75	5.00	5.00	5.12

Chemical dispersants increase the concentration of all the oil components in the water phase. The concentration of naphthalene was increased by 7.90 to 9.20 times during the test period. The concentration of fluorene was increased by 6.70 to 8.27 times. Kuhl et al. (2013) noticed a greater than 10 fold increase of PAH concentration in seawater due to the addition of chemical dispersants. The Kuhl et al. (2013) experiments were done using seawater in the range of 4 to 18 ppt salinity and at the temperature range of 16.4 ^{o}C to 21.1 ^{o}C.

The concentration of dibenzothiophene and phenanthrene increased by a factor of approximately 20. The larger PAHs, chrysene and pyrene, indicated ratios of 19.59 ± 0.83 to 23.43 ± 0.91 and 22.78 ± 1.03 to 29.52 ± 0.98 respectively. That indicates higher

concentrations of larger PAHs in water with the application of dispersants and more bio-available in dispersed form. Fuller et al. (2004) noted that the oil in CEWAF is principally available in the form of colloidal micelles rather than in dissolved form.

The ratios of larger PAHs decreased significantly with time. That reflects the slower dissolution in WAF while the concentrations in CEWAF were constant over the time. Phenol indicated a concentration increase of greater than five times relative to WAF. This was the smallest ratio compared to the others.

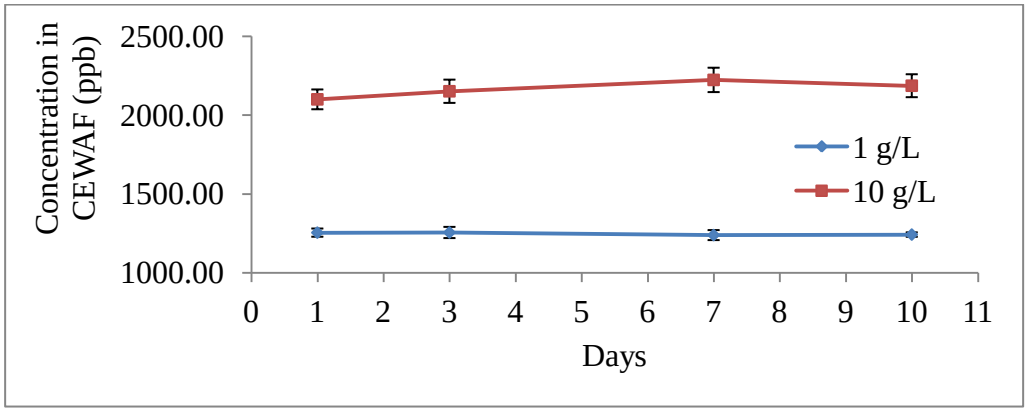
The concentrations of larger PAHs, which were previously found to be less available in WAF, were high in seawater with the application of dispersants. Since these larger PAHs are more resistant to weathering they can be more persistent in the ocean resulting long term impacts. According to a number of studies, the chemical dispersion can result in short term acute toxicity to pelagic organism as it increases the oil concentration in water column (Wolfe et al., 2001).

4.3.2 The effect of the time and oil loading on oil partitioning in CEWAF

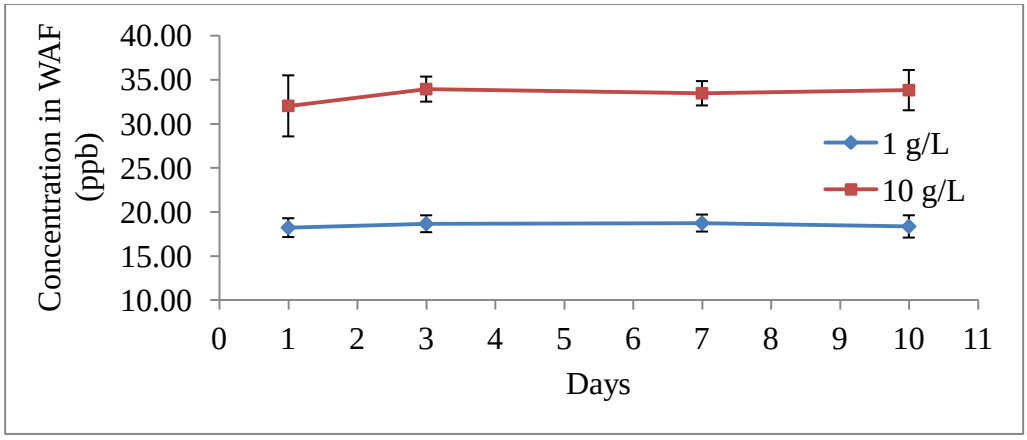
The partitioning behaviour of oil was observed by analyzing CEWAF with time. The study was carried out at two oil loadings: 1 g/L and 10 g/L. The results are shown in Figure 4-3. The highest concentration was recorded for naphthalene which dominated in WAF as well. The second highest concentration was measured for phenol throughout the test period and at both the oil loadings. The concentrations of naphthalene and phenol approximately doubled as the oil loading increased from 1 g/L to 10 g/L. Phenanthrene

was the third most abundant PAH at both oil loadings. The concentrations of all the other PAHs remained in the range of 18 to 22 ppb at 1 g/L oil loading. The concentrations increased as oil loading was increased to 10 g/L.

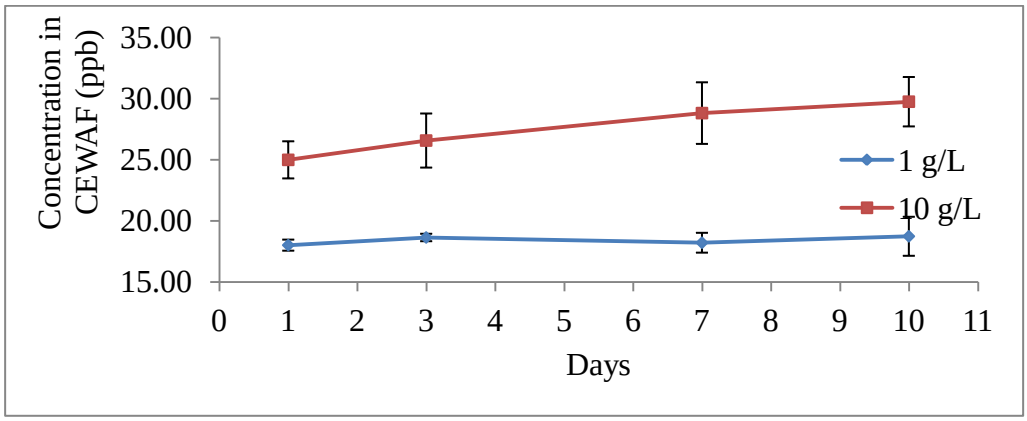
Figure 4-3 shows concentrations of each analyte as a function of time. All concentrations were constant with time at both oil loadings. Dibenzothiophene indicated a slight increase in concentration with time only in CEWAF of 10 g/L oil loading. However, this is insignificant, given the errors of measurement.



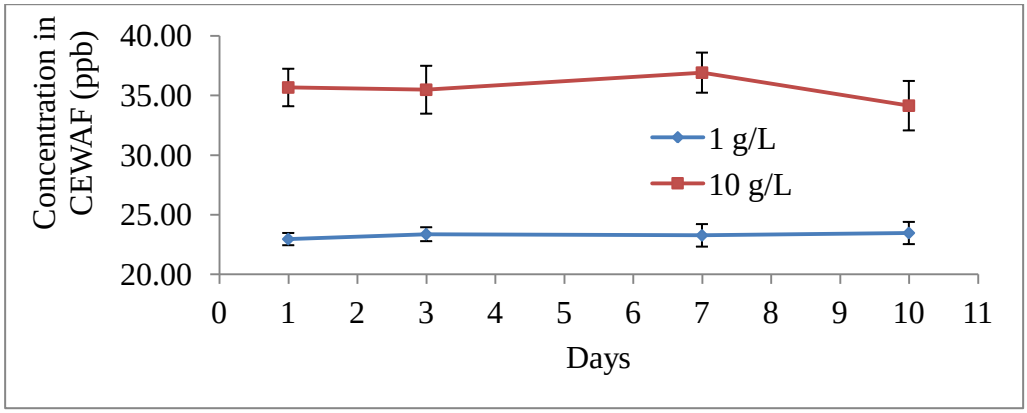
(a) Naphthalene



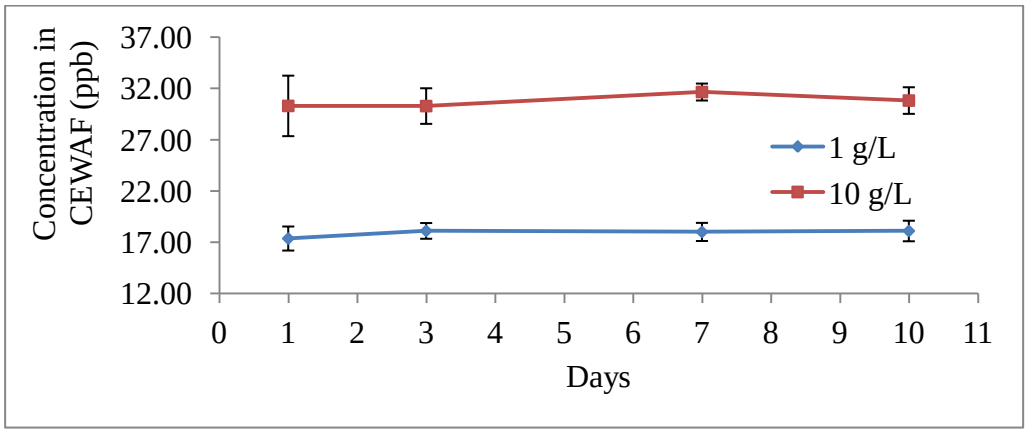
(b) Fluorene



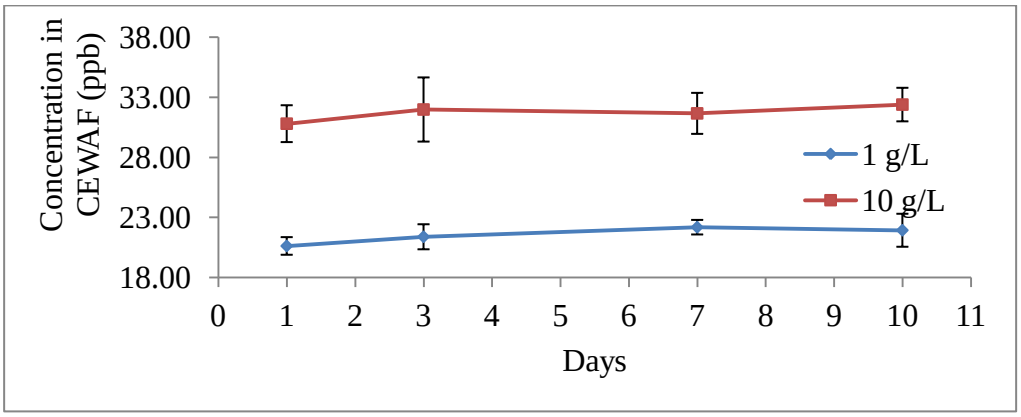
(c) Dibenzothiophene



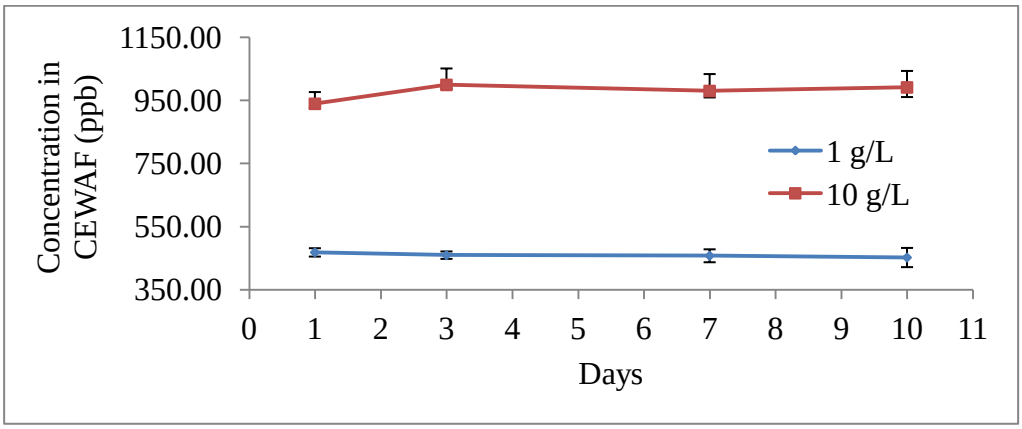
(d) Phenanthrene



(e) Chrysene



(f) Pyrene

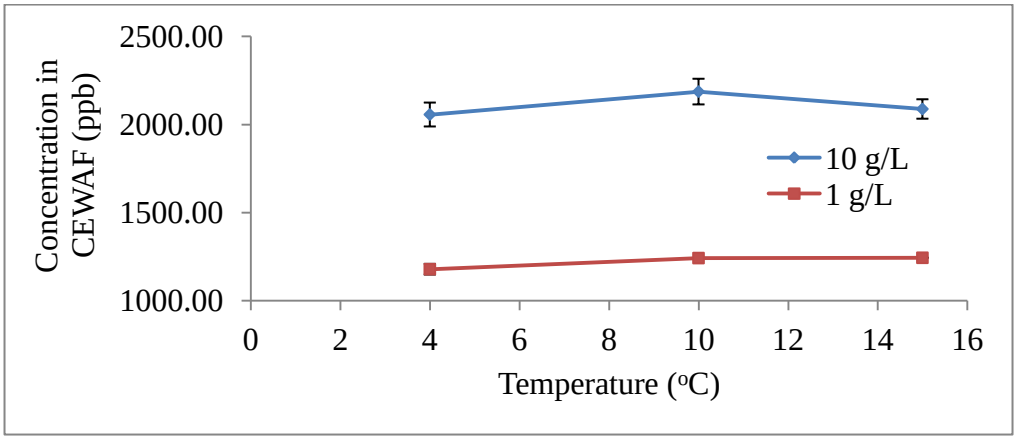


(g) Phenol

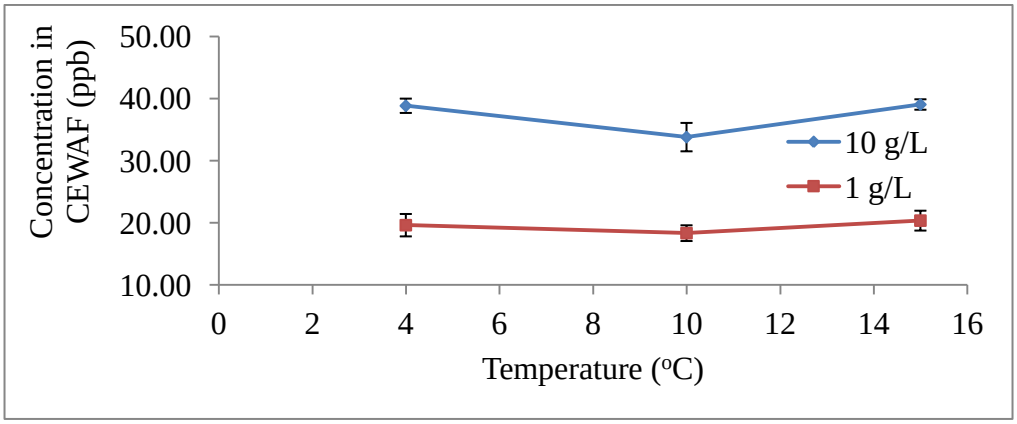
Figure 4-3: Concentration of (a) naphthalene, (b) fluorene, (c) dibenzothiophene, (d) phenanthrene, (e) pyrene, (f) chrysene and (g) phenol in CEWAF as a function of time at 1g/L and 10 g/L oil loadings at 10 ^{o}C temperature

4.3.3 Effect of temperature

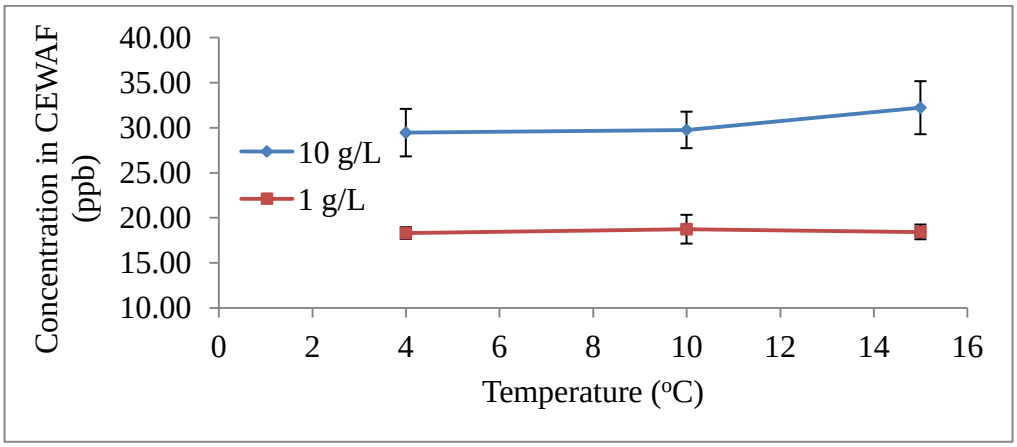
CEWAF experiments were carried out at three different temperatures: 4 ^{o}C, 10 ^{o}C and 15 ^{o}C to study the effect of the temperature on CEWAF concentrations. Figure 4-4 shows the variations of the each analyte concentration as a function of temperature at two oil loadings. All the analytes indicated constant concentrations over the temperature range. Therefore temperature did not have any significant influence on the concentrations of analytes in CEWAF.



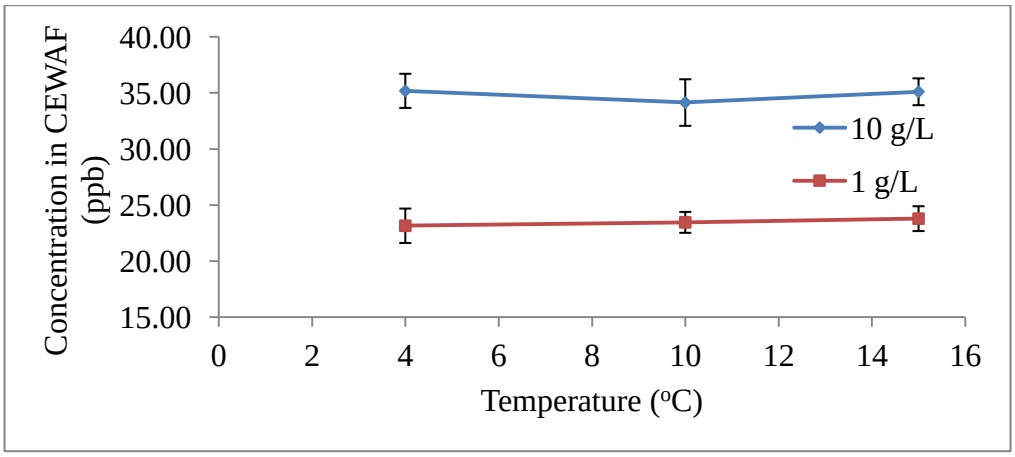
(a) Naphthalene



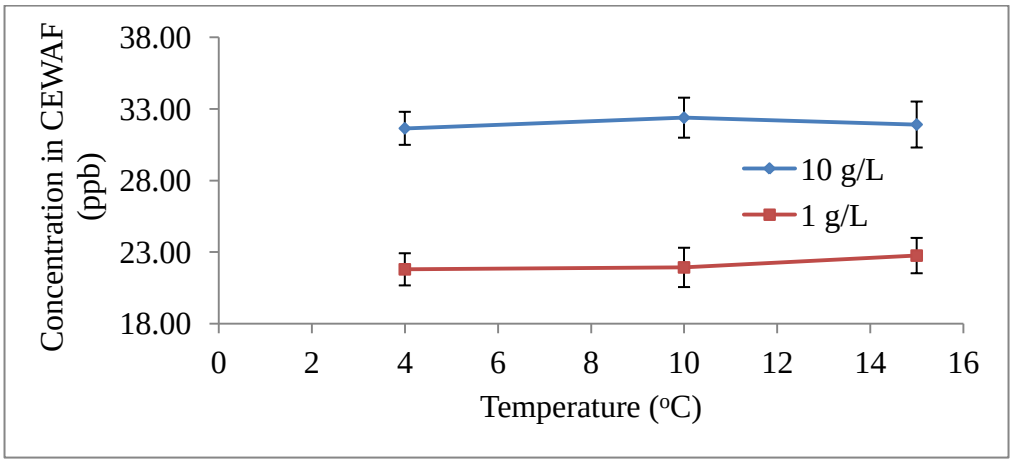
(b) Fluorene



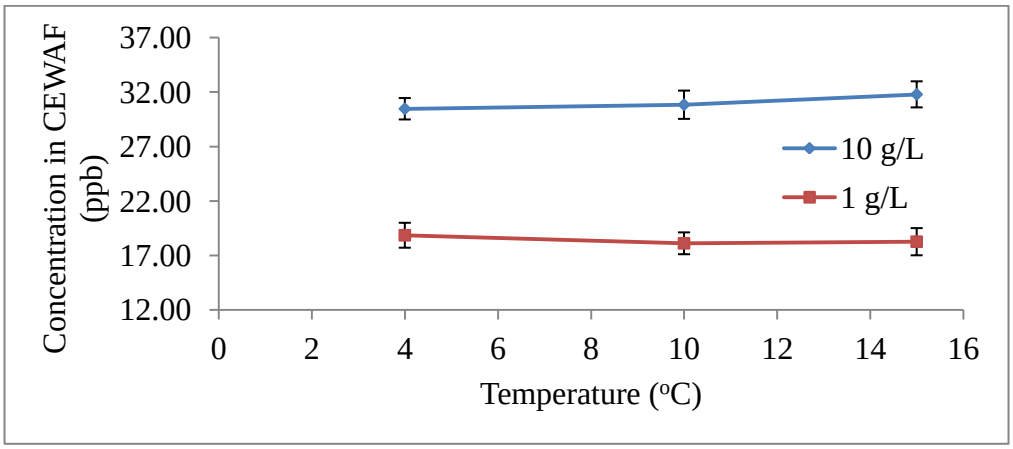
(c) Dibenzothiophene



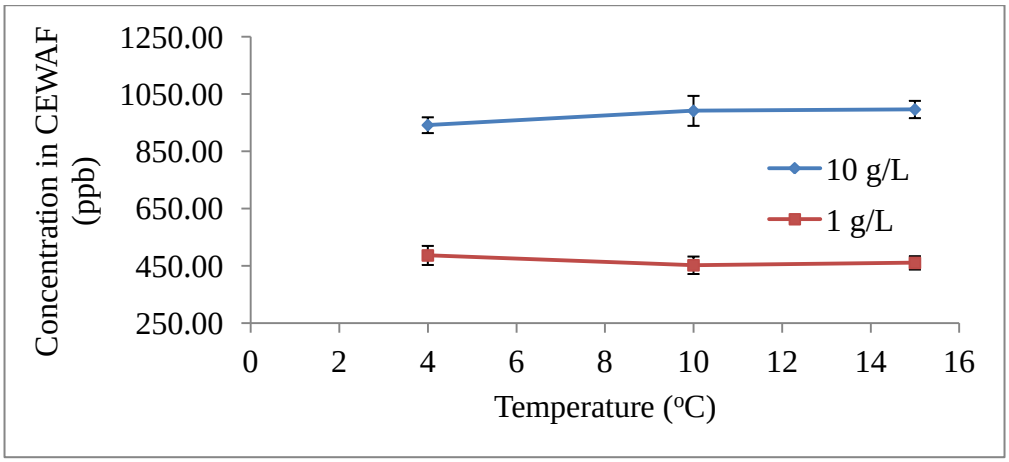
(d) Phenanthrene



(e) Pyrene



(f) Chrysene



(g) Phenol

Figure 4-4: Concentration of (a) naphthalene, (b) fluorene, (c) dibenzothiophene, (d) phenanthrene, (e) pyrene, (f) chrysene and (g) phenol in day ten CEWAF as a function of temperature at 1g/L and 10 g/L oil loadings

Figure 4-5 shows the TPH concentration in CEWAF as a function of time at two oil loadings, 1g/L and 10 g/L. Similar to previous WAF study, the TPH remained constant over the test period. TPH increased as the oil loading increased.

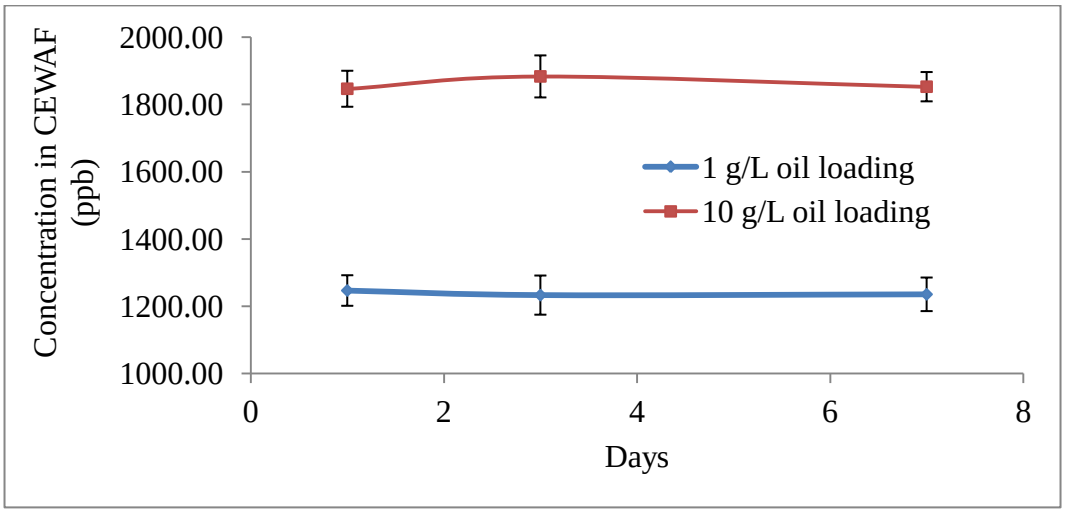


Figure 4-5: TPH concentration in CEWAF as a function of time at two different oil loadings at 10 ^{o}C

4.4 Conclusions

Chemical dispersants increased the availability of oil in seawater. More oil was dispersed into the water column with the help of mixing energy. Therefore the amount of the dispersed oil fraction increased significantly which resulted higher concentrations of PAHs and phenols in the CEWAF. The less soluble larger PAHs such as chrysene and pyrene indicated the largest concentration gain in CEWAF compared to the smaller PAHs. None of the target oil component indicated any change of concentration with time over the test period. No significant change in concentration was observed with temperature (from 4 to 15 ^{o}C). TPH concentration also remained constant over the test period.

Application of chemical dispersants, as an oil spill mitigation technique, reduces the risk of shore line and coastal surface contamination. However, chemical dispersants can increase a short term acute toxicity to the sea life as it increases the oil partitioning into the seawater column which results higher bioavailability of oil. According to the above finding the bioavailability of weather-resistant larger PAHs increased significantly and that could lead to a persistent risk of contamination of seawater. Therefore, the fate of an oil spill which has been treated by chemical dispersants can be even harmful to the ocean life.

5. Summary and Future Work

This study investigated the behaviour of spilled oil in harsh offshore environment by deploying laboratory scale oil spill experiments. The partitioning of some selected oil components that are considered to be potentially toxic to the aquatic life was studied as a function of time, temperature and oil loading to determine the fate of an oil spill.

Chapter one provided a review of the oil spill studies that were done to determine the oil pollutants and their behaviour in the ocean. Benzene, toluene, ethylbenzene and xylene (BTEX), polycyclic aromatic hydrocarbons (PAHs) and phenols were identified as the basic pollutants in terms of their bioavailability, persistent and potential toxicity to the marine life. The factors that involve in deciding the fate of oil were identified based on the results obtained in previous studies. An oil spill mitigation technique, the application of chemical dispersants, was discussed based on the information in the literature. This review highlighted that the information available in colder conditions were still lacking and more studies were needed to fill the gaps.

Chapter two provided the analysis of crude oil obtained from Newfoundland and Labrador offshore oil fields. Some of the physical properties were first measured to determine the type and characteristics of the oil. The concentrations of target analytes were measured in oil.

Chapter three was on the analysis of the water accommodated fraction (WAF) of oil. The behaviour of the target oil components were studied as a function of time (up to ten days), temperature (4-15 ^{o}C) and oil loading (1-10 g/L). Smaller ringed PAHs and phenols were more soluble in seawater and the partitioning of larger PAHs was slow.

Total petroleum hydrocarbon (TPH) measured as a baseline integrated concentration of alkanes from C8 to C40 and was constant over the test period. TPH did not correlate well to the other analytes studied and remained constant over the test period while the concentrations of others changed.

Chapter four presented the study of chemically enhanced water accommodated fraction (CEWAF) of oil. The effect of chemical dispersants on oil partitioning was studied as a function of all the factors considered in the WAF analysis. Results showed that chemical dispersant significantly increased the availability of all the target oil components in seawater. The information gathered at colder conditions would be helpful in future oil spill mitigation and remediation work.

Recommendations for future work are as follows;

- Studying a wider range of target analytes including BTEX and alkylated phenols (Sawamura et al., 2001).
- This study considered only the water accommodated fraction of oil. The water soluble fraction (WSF) of oil can be determined by separating the dispersed oil fraction by mechanical separation methods such as centrifugation (Reitsma et al., 2013; Siron et al., 1993).
- Studying the pH of seawater as an indicator of oil removal. The correlation between pH and the concentration of phenol would be an interesting fact to be studied.

- As an extension to this study, factors such as light intensity, mixing energy, amount of chemical dispersants added can be studied to determine their effects on oil partitioning.
- Studying the partitioning behaviour of weathered oil (Barron and Ka'aihue, 2003).
- Repeating the experiment with natural seawater. Natural seawater should be filtered and sterilized before using to minimize the biodegradation during the test.

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Appendices

Appendix A: Compositions of the four samples prepared to determine the concentrations of target analytes in WAF by standard addition technique

Component	Sample # 1 (mL)	Sample # 2 (mL)	Sample # 3 (mL)	Sample # 4 (mL)
Volume of SS (V_s)	0	1	2	3
Volume of oil sample (V_x)	3	3	3	3
Make-up DCM volume	3	2	1	0
Total volume (V_T)	6	6	6	6

Appendix B: Compositions of the four samples prepared to determine the concentrations of target analytes in CEWAF by standard addition technique

Component	Sample # 1 (mL)	Sample # 2 (mL)	Sample # 3 (mL)	Sample # 4 (mL)
Volume of SS (V_s)	0	1	2	3
Volume of oil sample (V_x)	2	2	2	2
Make-up DCM volume	4	3	2	1
Total volume (V_T)	6	6	6	6

Appendix C: The errors associated with the GC analysis of a standard sample of ppb range concentration

Analytes	Anticipated concentration in the standard (ppb)	Detected concentration by GC-MS (ppb)	% Error
Acenaphthene-d_{10} (IS)	100.23 ± 1.23	88.38 ± 2.21	11.82
Naphthalene	100.19 ± 1.37	88.13 ± 2.34	12.04
Fluorene	10.23 ± 1.08	8.68 ± 1.34	15.11
Dibenzothiophene	10.13 ± 1.12	8.23 ± 1.63	18.78
Phenanthrene	10.31 ± 1.31	8.77 ± 1.24	14.89
Chrysene	10.13 ± 1.17	8.42 ± 1.20	16.88
Pyrene	10.18 ± 1.08	8.38 ± 1.37	17.67
Phenol	100.21 ± 1.62	80.02 ± 2.85	20.15

Appendix D: The GC method of PAHs and phenol analysis

```
                              INSTRUMENT CONTROL PARAMETERS
                              -----------------------------

================================================================================
                                 6890 GC METHOD
================================================================================

OVEN
   Initial temp:  40 'C (On)                  Maximum temp:  320 'C
   Initial time:  1.00 min                    Equilibration time:  0.50 min
   Ramps:
      #  Rate  Final temp  Final time
      1 30.00      130        2.00
      2 24.00      200        0.00
      3  8.00      220        0.00
      4 24.00      300        1.50
      5   0.0(Off)
   Post temp:  0 'C
   Post time:  0.00 min
   Run time:  16.25 min

FRONT INLET (SPLIT/SPLITLESS)              BACK INLET (UNKNOWN)
   Mode:  Splitless
   Initial temp:  280 'C (On)
   Pressure:  9.99 psi (On)
   Purge flow:  50.0 mL/min
   Purge time:  1.50 min
   Total flow:  54.5 mL/min
   Gas saver:  On
   Saver flow:  20.0 mL/min
   Saver time:  1.50 min
   Gas type:  Helium

COLUMN 1                                   COLUMN 2
   Capillary Column                           (not installed)
   Model Number:  Agilent 122-5532
   DB-5ms, 0.25mm * 30m * 0.25um
   Max temperature:  350 'C
   Nominal length:  30.0 m
   Nominal diameter:  250.00 um
   Nominal film thickness:  0.25 um
   Mode:  constant flow
   Initial flow:  1.3 mL/min
   Nominal init pressure:  10.00 psi
   Average velocity:  41 cm/sec
   Inlet:  Front Inlet
   Outlet:  MSD
   Outlet pressure:  vacuum

FRONT DETECTOR ()                          BACK DETECTOR ()

SIGNAL 1                                   SIGNAL 2
   Data rate:  20 Hz                          Data rate:  20 Hz
   Type:  test plot                           Type:  test plot
   Save Data:  Off                            Save Data:  Off
   Zero:  0.0 (Off)                           Zero:  0.0 (Off)
   Range:  0                                  Range:  0
   Fast Peaks:  Off                           Fast Peaks:  Off
   Attenuation:  0                            Attenuation:  0

COLUMN COMP 1                              COLUMN COMP 2
   (No Detectors Installed)                   (No Detectors Installed)

THERMAL AUX 2
   Use:  MSD Transfer Line Heater
   Description:
```

```
   Initial temp:  300 'C (On)
   Initial time:  0.00 min
      #  Rate  Final temp  Final time
      1   0.0(Off)

                                        POST RUN
                                           Post Time: 0.00 min

TIME TABLE
   Time       Specifier                      Parameter & Setpoint

                              7673 Injector


     Front Injector:
        Sample Washes                 0
        Sample Pumps                  6
        Injection Volume            1.0 microliters
        Syringe Size               10.0 microliters
        PostInj Solvent A Washes      3
        PostInj Solvent B Washes      3
        Viscosity Delay               0 seconds
        Plunger Speed              Fast
        PreInjection Dwell         0.00 minutes
        PostInjection Dwell        0.00 minutes

     Back Injector:
No parameters specified

 Column 1 Inventory Number : 2
 Column 2 Inventory Number :

                                MS ACQUISITION PARAMETERS


General Information
------- -----------

Tune File                 : atune.u
Acquistion Mode           : SIM


MS Information
-- -----------

Solvent Delay             : 4.00 min

EM Absolute               : False
EM Offset                 : 0
Resulting EM Voltage      : 2223.5

[Sim Parameters]

GROUP 1
Group ID                  : Phenol
Resolution                : Low
Plot 1 Ion                : 66.0
Ions/Dwell In Group       (  Mass,  Dwell) (  Mass,  Dwell) (  Mass,  Dwell)
                          (  39.0,    100) (  66.0,    100) (  94.0,    100)

GROUP 2
Group ID                  : Naphthalene
Resolution                : Low
Group Start Time          : 6.10
Plot 1 Ion                : 127.0
Ions/Dwell In Group       (  Mass,  Dwell) (  Mass,  Dwell) (  Mass,  Dwell)
                          ( 127.0,    100) ( 128.0,    100) ( 129.0,    100)
```

```
GROUP 3
Group ID                : Ace-naph-D10
Resolution              : Low
Group Start Time        : 8.75
Plot 1 Ion              : 160.0
Ions/Dwell In Group     (  Mass,  Dwell) (  Mass,  Dwell) (  Mass,  Dwell)
                        ( 160.0,    100) ( 162.0,    100) ( 163.0,    100)
                        ( 164.0,    100)

GROUP 4
Group ID                : Fluorene
Resolution              : Low
Group Start Time        : 9.45
Plot 1 Ion              : 165.0
Ions/Dwell In Group     (  Mass,  Dwell) (  Mass,  Dwell) (  Mass,  Dwell)
                        ( 165.0,    100) ( 166.0,    100) ( 167.0,    100)
                        ( 168.0,    100)

GROUP 5
Group ID                : Dibenzothiophen
Resolution              : Low
Group Start Time        : 10.76
Plot 1 Ion              : 139.0
Ions/Dwell In Group     (  Mass,  Dwell) (  Mass,  Dwell) (  Mass,  Dwell)
                        ( 139.0,    100) ( 184.0,    100) ( 185.0,    100)

GROUP 6
Group ID                : Phenanthrene
Resolution              : Low
Group Start Time        : 10.96
Plot 1 Ion              : 89.0
Ions/Dwell In Group     (  Mass,  Dwell) (  Mass,  Dwell) (  Mass,  Dwell)
                        (  89.0,    100) ( 176.0,    100) ( 178.0,    100)
                        ( 179.0,    100)

GROUP 7
Group ID                : Pyrene
Resolution              : Low
Group Start Time        : 13.25
Plot 1 Ion              : 101.0
Ions/Dwell In Group     (  Mass,  Dwell) (  Mass,  Dwell) (  Mass,  Dwell)
                        ( 101.0,    100) ( 200.0,    100) ( 202.0,    100)
                        ( 203.0,    100)

GROUP 8
Group ID                : Chrysene
Resolution              : Low
Group Start Time        : 14.85
Plot 1 Ion              : 226.0
Ions/Dwell In Group     (  Mass,  Dwell) (  Mass,  Dwell) (  Mass,  Dwell)
                        ( 226.0,    100) ( 227.0,    100) ( 228.0,    100)
                        ( 229.0,    100)

[MSZones]

MS Quad                 : 150 C   maximum 200 C
MS Source               : 230 C   maximum 250 C

                    END OF MS ACQUISITION PARAMETERS


                      TUNE PARAMETERS
                    ----------------------------

 EMISSION     :      34.610
 ENERGY       :      69.922
```

```
 REPELLER     :      16.385
 IONFOCUS     :      81.616
 ENTRANCE_LE  :      21.000
 EMVOLTS      :    2223.529
 AMUGAIN      :    2089.000
 AMUOFFSET    :     127.000
 FILAMENT     :       1.000
 DCPOLARITY   :       1.000
 ENTLENSOFFS  :      14.557
MASSGAIN      :    -312.000
MASSOFFSET    :      -9.000

                    END OF TUNE PARAMETERS
                  -----------------------------------


                    END OF INSTRUMENT CONTROL PARAMETERS
                    -----------------------------------
```

Appendix E: The GC method of TPH analysis

```
                              TOPLEVEL PARAMETERS
                              -------------------

Method Information For: C:\MSDCHEM\1\METHODS\KWITHANATPH1.M

Method Sections To Run:

   ( ) Save Copy of Method With Data
   ( ) MSTOP               Pre-Run Cmd/Macro  =
   ( ) Instrument Control  Pre-Run Cmd/Macro  =
   ( ) Data Analysis       Pre-Run Cmd/Macro  =
   (X) Data Acquisition
   (X) Data Analysis
   ( ) MSTOP               Post-Run Cmd/Macro =
   ( ) Instrument Control  Post-Run Cmd/Macro =
   ( ) Data Analysis       Post-Run Cmd/Macro =
Method Comments:
  Method for TPH1


                              END OF TOPLEVEL PARAMETERS
                              --------------------------




                              INSTRUMENT CONTROL PARAMETERS
                              -----------------------------

================================================================================
                               6890 GC METHOD
================================================================================

OVEN
   Initial temp:  40 'C (On)                  Maximum temp:  320 'C
   Initial time:  2.00 min                    Equilibration time:  0.50 min
   Ramps:
      #  Rate  Final temp  Final time
      1 12.00      300        4.00
      2  5.00      315       12.00
      3   0.0(Off)
   Post temp:  0 'C
   Post time:  0.00 min
   Run time:  42.67 min

FRONT INLET (SPLIT/SPLITLESS)           BACK INLET (UNKNOWN)
   Mode:  Splitless
   Initial temp:  280 'C (On)
   Pressure:  9.99 psi (On)
   Purge flow:  50.0 mL/min
   Purge time:  1.50 min
   Total flow:  54.5 mL/min
   Gas saver:  On
   Saver flow:  20.0 mL/min
   Saver time:  1.50 min
   Gas type:  Helium

COLUMN 1                                COLUMN 2
   Capillary Column                        (not installed)
   Model Number:  Agilent 122-5532
   DB-5ms, 0.25mm * 30m * 0.25um
   Max temperature:  350 'C
   Nominal length:  30.0 m
   Nominal diameter:  250.00 um
   Nominal film thickness:  0.25 um
   Mode:  constant flow
   Initial flow:  1.3 mL/min

Method: KWITHANATPH1.M          Thu Aug 14 09:40:40 2014          Page: 1
```

```
   Nominal init pressure:  10.00 psi
   Average velocity:  41 cm/sec
   Inlet:  Front Inlet
   Outlet:  MSD
   Outlet pressure:  vacuum

FRONT DETECTOR ()                          BACK DETECTOR ()

SIGNAL 1                                   SIGNAL 2
   Data rate:  20 Hz                          Data rate:  20 Hz
   Type:  test plot                           Type:  test plot
   Save Data:  Off                            Save Data:  Off
   Zero:  0.0 (Off)                           Zero:  0.0 (Off)
   Range:  0                                  Range:  0
   Fast Peaks:  Off                           Fast Peaks:  Off
   Attenuation:  0                            Attenuation:  0

COLUMN COMP 1                              COLUMN COMP 2
   (No Detectors Installed)                   (No Detectors Installed)

THERMAL AUX 2
   Use:  MSD Transfer Line Heater
   Description:
   Initial temp:  300 'C (On)
   Initial time:  0.00 min
      #  Rate  Final temp  Final time
      1   0.0(Off)

                                           POST RUN
                                              Post Time: 0.00 min

TIME TABLE
   Time       Specifier                        Parameter & Setpoint

                              7673 Injector


     Front Injector:
        Sample Washes                0
        Sample Pumps                 6
        Injection Volume           1.0 microliters
        Syringe Size              10.0 microliters
        PostInj Solvent A Washes     3
        PostInj Solvent B Washes     3
        Viscosity Delay              0 seconds
        Plunger Speed             Fast
        PreInjection Dwell        0.00 minutes
        PostInjection Dwell       0.00 minutes

     Back Injector:
No parameters specified

 Column 1 Inventory Number : 2
 Column 2 Inventory Number :

                              MS ACQUISITION PARAMETERS


General Information
------- -----------

Tune File                : atune.u
Acquistion Mode          : SIM


MS Information
-- -----------

Solvent Delay            : 4.00 min

Method: KWITHANATPH1.M           Thu Aug 14 09:40:40 2014           Page: 2
```

```
EM Absolute              : False
EM Offset                : 0
Resulting EM Voltage     : 1847.1

[Sim Parameters]

GROUP 1
Group ID                 : Octane
Resolution               : Low
Plot 1 Ion               : 43.0
Ions/Dwell In Group      (  Mass,  Dwell) (  Mass,  Dwell) (  Mass,  Dwell)
                         (  41.0,    100) (  43.0,    100) (  57.0,    100)
                         (  71.0,    100) (  85.0,    100)

GROUP 2
Group ID                 : Decane
Resolution               : Low
Group Start Time         : 7.45
Plot 1 Ion               : 43.0
Ions/Dwell In Group      (  Mass,  Dwell) (  Mass,  Dwell) (  Mass,  Dwell)
                         (  29.0,    100) (  41.0,    100) (  43.0,    100)
                         (  57.0,    100) (  71.0,    100)

GROUP 3
Group ID                 : Dodecane
Resolution               : Low
Group Start Time         : 10.20
Plot 1 Ion               : 41.0
Ions/Dwell In Group      (  Mass,  Dwell) (  Mass,  Dwell) (  Mass,  Dwell)
                         (  41.0,    100) (  43.0,    100) (  57.0,    100)
                         (  71.0,    100) (  85.0,    100)

GROUP 4
Group ID                 : Tetradecane
Resolution               : Low
Group Start Time         : 12.50
Plot 1 Ion               : 41.0
Ions/Dwell In Group      (  Mass,  Dwell) (  Mass,  Dwell) (  Mass,  Dwell)
                         (  41.0,    100) (  43.0,    100) (  57.0,    100)
                         (  71.0,    100) (  85.0,    100)

GROUP 5
Group ID                 : Acenaph-d10
Resolution               : Low
Group Start Time         : 13.55
Plot 1 Ion               : 80.0
Ions/Dwell In Group      (  Mass,  Dwell) (  Mass,  Dwell) (  Mass,  Dwell)
                         (  80.0,    100) ( 160.0,    100) ( 162.0,    100)
                         ( 163.0,    100) ( 164.0,    100)

GROUP 6
Group ID                 : Hexadecane
Resolution               : Low
Group Start Time         : 14.60
Plot 1 Ion               : 41.0
Ions/Dwell In Group      (  Mass,  Dwell) (  Mass,  Dwell) (  Mass,  Dwell)
                         (  41.0,    100) (  43.0,    100) (  57.0,    100)
                         (  71.0,    100) (  85.0,    100)

GROUP 7
Group ID                 : Octadecane
Resolution               : Low
Group Start Time         : 16.45
Plot 1 Ion               : 41.0
Ions/Dwell In Group      (  Mass,  Dwell) (  Mass,  Dwell) (  Mass,  Dwell)
                         (  41.0,    100) (  43.0,    100) (  57.0,    100)
                         (  71.0,    100) (  85.0,    100)

GROUP 8
```

```
Group ID                : O-Terphenyl
Resolution              : Low
Group Start Time        : 17.35
Plot 1 Ion              : 215.0
Ions/Dwell In Group     (  Mass,  Dwell) (  Mass,  Dwell) (  Mass,  Dwell)
                        ( 215.0,    100) ( 228.0,    100) ( 229.0,    100)
                        ( 230.0,    100) ( 231.0,    100)

GROUP 9
Group ID                : Eicosane
Resolution              : Low
Group Start Time        : 18.20
Plot 1 Ion              : 41.0
Ions/Dwell In Group     (  Mass,  Dwell) (  Mass,  Dwell) (  Mass,  Dwell)
                        (  41.0,    100) (  43.0,    100) (  55.0,    100)
                        (  57.0,    100) (  71.0,    100)

GROUP 10
Group ID                : Docosane
Resolution              : Low
Group Start Time        : 19.70
Plot 1 Ion              : 41.0
Ions/Dwell In Group     (  Mass,  Dwell) (  Mass,  Dwell) (  Mass,  Dwell)
                        (  41.0,    100) (  43.0,    100) (  57.0,    100)
                        (  71.0,    100) (  85.0,    100)

GROUP 11
Group ID                : Tetracosane
Resolution              : Low
Group Start Time        : 21.15
Plot 1 Ion              : 43.0
Ions/Dwell In Group     (  Mass,  Dwell) (  Mass,  Dwell) (  Mass,  Dwell)
                        (  41.0,    100) (  43.0,    100) (  57.0,    100)
                        (  71.0,    100) (  85.0,    100)

GROUP 12
Group ID                : Hexacosane
Resolution              : Low
Group Start Time        : 22.45
Plot 1 Ion              : 43.0
Ions/Dwell In Group     (  Mass,  Dwell) (  Mass,  Dwell) (  Mass,  Dwell)
                        (  43.0,    100) (  55.0,    100) (  57.0,    100)
                        (  71.0,    100) (  85.0,    100)

GROUP 13
Group ID                : Octacosane
Resolution              : Low
Group Start Time        : 23.70
Plot 1 Ion              : 43.0
Ions/Dwell In Group     (  Mass,  Dwell) (  Mass,  Dwell) (  Mass,  Dwell)
                        (  43.0,    100) (  55.0,    100) (  57.0,    100)
                        (  71.0,    100) (  85.0,    100)

GROUP 14
Group ID                : Triacontane
Resolution              : Low
Group Start Time        : 25.00
Plot 1 Ion              : 43.0
Ions/Dwell In Group     (  Mass,  Dwell) (  Mass,  Dwell) (  Mass,  Dwell)
                        (  43.0,    100) (  55.0,    100) (  57.0,    100)
                        (  71.0,    100) (  85.0,    100)

GROUP 15
Group ID                : Dotriacontane
Resolution              : Low
Group Start Time        : 26.80
Plot 1 Ion              : 43.0
Ions/Dwell In Group     (  Mass,  Dwell) (  Mass,  Dwell) (  Mass,  Dwell)
                        (  43.0,    100) (  55.0,    100) (  57.0,    100)
                        (  71.0,    100) (  85.0,    100)

Method: KWITHANATPH1.M          Thu Aug 14 09:40:40 2014          Page: 4
```

```
GROUP 16
Group ID                : Tetratriacontan
Resolution              : Low
Group Start Time        : 29.15
Plot 1 Ion              : 43.0
Ions/Dwell In Group     (  Mass,  Dwell) (  Mass,  Dwell) (  Mass,  Dwell)
                        (  43.0,    100) (  55.0,    100) (  57.0,    100)
                        (  71.0,    100) (  85.0,    100)

GROUP 17
Group ID                : Hexatriacontane
Resolution              : Low
Group Start Time        : 31.55
Plot 1 Ion              : 43.0
Ions/Dwell In Group     (  Mass,  Dwell) (  Mass,  Dwell) (  Mass,  Dwell)
                        (  43.0,    100) (  55.0,    100) (  57.0,    100)
                        (  71.0,    100) (  85.0,    100)

GROUP 18
Group ID                : Octatriacontane
Resolution              : Low
Group Start Time        : 34.60
Plot 1 Ion              : 41.0
Ions/Dwell In Group     (  Mass,  Dwell) (  Mass,  Dwell) (  Mass,  Dwell)
                        (  41.0,    100) (  43.0,    100) (  55.0,    100)
                        (  57.0,    100) (  71.0,    100) (  85.0,    100)

GROUP 19
Group ID                : Tetracontane
Resolution              : Low
Group Start Time        : 39.00
Plot 1 Ion              : 41.0
Ions/Dwell In Group     (  Mass,  Dwell) (  Mass,  Dwell) (  Mass,  Dwell)
                        (  41.0,    100) (  43.0,    100) (  55.0,    100)
                        (  57.0,    100) (  71.0,    100) (  85.0,    100)

[MSZones]

MS Quad                 : 150 C   maximum 200 C
MS Source               : 230 C   maximum 250 C

                    END OF MS ACQUISITION PARAMETERS

                  END OF INSTRUMENT CONTROL PARAMETERS
                  ------------------------------------
```

Appendix F: The GC method of alkylated phenol analysis

```
                              TOPLEVEL PARAMETERS
                              -------------------

Method Information For: C:\MSDCHEM\1\METHODS\KW_PHENOLS_1.M

Method Sections To Run:

   ( ) Save Copy of Method With Data
   ( ) MSTOP               Pre-Run Cmd/Macro  =
   ( ) Instrument Control  Pre-Run Cmd/Macro  =
   ( ) Data Analysis       Pre-Run Cmd/Macro  =
   (X) Data Acquisition
   (X) Data Analysis
   ( ) MSTOP               Post-Run Cmd/Macro =
   ( ) Instrument Control  Post-Run Cmd/Macro =
   ( ) Data Analysis       Post-Run Cmd/Macro =
Method Comments:
  This is the default method


                              END OF TOPLEVEL PARAMETERS
                              --------------------------




                              INSTRUMENT CONTROL PARAMETERS
                              -----------------------------

================================================================================
                               6890 GC METHOD
================================================================================

OVEN
   Initial temp:  40 'C (On)                  Maximum temp:  350 'C
   Initial time:  1.00 min                    Equilibration time:  0.50 min
   Ramps:
      #  Rate  Final temp  Final time
      1 22.00      120        0.00
      2 12.00      170        0.00
      3 25.00      275        0.00
      4   0.0(Off)
   Post temp:  0 'C
   Post time:  0.00 min
   Run time:  13.00 min

FRONT INLET (SPLIT/SPLITLESS)              BACK INLET (UNKNOWN)
   Mode:  Splitless
   Initial temp:  280 'C (On)
   Pressure:  8.75 psi (On)
   Purge flow:  50.0 mL/min
   Purge time:  1.50 min
   Total flow:  54.4 mL/min
   Gas saver:  On
   Saver flow:  20.0 mL/min
   Saver time:  2.00 min
   Gas type:  Helium

COLUMN 1                                   COLUMN 2
   Capillary Column                           (not installed)
   Model Number:  Agilent 122-5532
   DB-5ms, 0.25mm * 30m * 0.25um
   Max temperature:  350 'C
   Nominal length:  30.0 m
   Nominal diameter:  250.00 um
   Nominal film thickness:  0.25 um
   Mode:  constant flow

Method: KW_PHENOLS_1.M          Fri Sep 04 12:20:12 2015          Page: 1
```

```
   Initial flow:  1.2 mL/min
   Nominal init pressure:  8.75 psi
   Average velocity:  39 cm/sec
   Inlet:  Front Inlet
   Outlet:  MSD
   Outlet pressure:  vacuum

FRONT DETECTOR ()                          BACK DETECTOR ()

SIGNAL 1                                   SIGNAL 2
   Data rate:  20 Hz                          Data rate:  20 Hz
   Type:  test plot                           Type:  test plot
   Save Data:  Off                            Save Data:  Off
   Zero:  0.0 (Off)                           Zero:  0.0 (Off)
   Range:  0                                  Range:  0
   Fast Peaks:  Off                           Fast Peaks:  Off
   Attenuation:  0                            Attenuation:  0

COLUMN COMP 1                              COLUMN COMP 2
   (No Detectors Installed)                   (No Detectors Installed)

THERMAL AUX 2
   Use:  MSD Transfer Line Heater
   Description:
   Initial temp:  280 'C (On)
   Initial time:  0.00 min
      #  Rate  Final temp  Final time
      1   0.0(Off)

                                           POST RUN
                                              Post Time: 0.00 min

TIME TABLE
   Time       Specifier                        Parameter & Setpoint

                              7673 Injector


     Front Injector:
        Sample Washes                 0
        Sample Pumps                  6
        Injection Volume            1.0 microliters
        Syringe Size               10.0 microliters
        PostInj Solvent A Washes      3
        PostInj Solvent B Washes      3
        Viscosity Delay               0 seconds
        Plunger Speed              Fast
        PreInjection Dwell         0.00 minutes
        PostInjection Dwell        0.00 minutes

     Back Injector:
No parameters specified

 Column 1 Inventory Number : 2
 Column 2 Inventory Number :

                                MS ACQUISITION PARAMETERS


General Information
------- -----------

Tune File                : ATUNE.U
Acquistion Mode          : SIM


MS Information
-- -----------


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```
Solvent Delay              : 4.00 min

EM Absolute                : False
EM Offset                  : 0
Resulting EM Voltage       : 2647.1

[Sim Parameters]

GROUP 1
Group ID                   : O-Cresol
Resolution                 : Low
Plot 1 Ion                 : 108.0
Ions/Dwell In Group        (  Mass,  Dwell) (  Mass,  Dwell) (  Mass,  Dwell)
                           (  77.0,    100) (  79.0,    100) ( 107.0,    100)
                           ( 108.0,    100)

GROUP 2
Group ID                   : m-Cresol
Resolution                 : Low
Group Start Time           : 5.65
Plot 1 Ion                 : 108.0
Ions/Dwell In Group        (  Mass,  Dwell) (  Mass,  Dwell) (  Mass,  Dwell)
                           (  77.0,    100) (  79.0,    100) ( 107.0,    100)
                           ( 108.0,    100)

GROUP 3
Group ID                   : 4-Ethylphenol
Resolution                 : Low
Group Start Time           : 6.48
Plot 1 Ion                 : 122.0
Ions/Dwell In Group        (  Mass,  Dwell) (  Mass,  Dwell) (  Mass,  Dwell)
                           (  77.0,    100) ( 107.0,    100) ( 108.0,    100)
                           ( 122.0,    100)

[MSZones]

MS Quad                    : 150 C   maximum 200 C
MS Source                  : 230 C   maximum 250 C

                             END OF MS ACQUISITION PARAMETERS

                           END OF INSTRUMENT CONTROL PARAMETERS
                           -----------------------------------




                           DATA ANALYSIS PARAMETERS
                           ------------------------

Method Name: C:\MSDCHEM\1\METHODS\KW_PHENOLS_1.M


Percent Report Settings
-----------------------

Sort By: Signal

Output Destination
    Screen:  No
    Printer: Yes
    File:    No

Integration Events: AutoIntegrate

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Appendix G: Chemical dispersant (COREXIT EC9500A) material data sheet

NALCO Environmental Solutions LLC

COREXIT® Ingredients

Several weeks ago, Nalco responded to US EPA requests by providing the agency with detailed formulation and ingredient information on our COREXIT® dispersants. We further agreed that this information could be shared with any other federal agency and with third party laboratories EPA has been using for its Gulf monitoring and assessment program to allow them to monitor any potential for risks to the environment or public health.

The table below outlines the same ingredient list for our COREXIT dispersants as provided to the EPA.

CAS #	Name	Common Day-to-Day Use Examples
1338-43-8	Sorbitan, mono-(9Z)-9-octadecenoate	Skin cream, body shampoo, emulsifier in juice
9005-65-6	Sorbitan, mono-(9Z)-9-octadecenoate, poly(oxy-1,2-ethanediyl) derivs.	Baby bath, mouth wash, face lotion, emulsifier in food
9005-70-3	Sorbitan, tri-(9Z)-9-octadecenoate, poly(oxy-1,2-ethanediyl) derivs	Body/Face lotion, tanning lotions
577-11-7	* Butanedioic acid, 2-sulfo-, 1,4-bis(2-ethylhexyl) ester, sodium salt (1:1)	Wetting agent in cosmetic products, gelatin, beverages
29911-28-2	Propanol, 1-(2-butoxy-1-methylethoxy)	Household cleaning products
64742-47-8	Distillates (petroleum), hydrotreated light	Air freshener, cleaner
111-76-2	** Ethanol, 2-butoxy	Cleaners

* Contains 2-Propanediol ** This chemical component (Ethanol, 2-butoxy-) is NOT included in the composition of COREXIT® 9500

COREXIT 9500 is the sole product we have been making for Gulf responders since the spill began. Limited quantities of COREXIT® 9527 may have been drawn from existing dispersant stockpiles from around the world. COREXIT 9500 does not include the ingredient 2-butoxy ethanol, an ingredient in COREXIT 9527.

Both COREXIT dispersants have been listed by the EPA as part of the National Contingency Plan for treating oil spills.

In addition, a May 2010 report by the Centers for Disease Control concluded that "because of the strict guidelines that must be followed to utilize dispersants, it is unlikely that the general public will be exposed (directly) to (the) product." The report further states that "ingredients are not considered to cause chemical sensitization; the dispersants contain proven, biodegradable and low toxicity surfactants."

Disclaimer: *COREXIT 9500 and COREXIT 9527 are on the U.S. Environmental Protection Agency's NCP Product Schedule. This*

HUMAN EXPOSURE CHARACTERIZATION :
Based on our recommended product application and personal protective equipment, the potential human exposure is: Low

9. PHYSICAL AND CHEMICAL PROPERTIES

PHYSICAL STATE	Liquid
APPEARANCE	Clear Hazy Amber
ODOR	Hydrocarbon
SPECIFIC GRAVITY	0.95 @ 60 °F / 15.6 °C
DENSITY	7.91 lb/gal
SOLUBILITY IN WATER	Miscible
pH (100 %)	6.2
VISCOSITY	177 cst @ 32 °F / 0 °C 70 cst @ 60 °F / 15.6 °C
POUR POINT	< -71 °F / < -57 °C
BOILING POINT	296 °F / 147 °C
VAPOR PRESSURE	15.5 mm Hg @ 100 °F / 37.8 °C

Note: These physical properties are typical values for this product and are subject to change.

10. STABILITY AND REACTIVITY

STABILITY :
Stable under normal conditions.

HAZARDOUS POLYMERIZATION :
Hazardous polymerization will not occur.

CONDITIONS TO AVOID :
Heat and sources of ignition including static discharges.

MATERIALS TO AVOID :
Contact with strong oxidizers (e.g. chlorine, peroxides, chromates, nitric acid, perchlorate, concentrated oxygen, permanganate) may generate heat, fires, explosions and/or toxic vapors.

HAZARDOUS DECOMPOSITION PRODUCTS :
Under fire conditions: Oxides of carbon, Oxides of sulfur

11. TOXICOLOGICAL INFORMATION

SENSITIZATION:
This product is not expected to be a sensitizer.